LIMITS OF FLAMMABILITY OF GASES AND VAPORS

BY H. F. COWARD AND G. W. JONES

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FOREWORD

This bulletin is the fourth edition of one of a series of publications issued as a result of cooperation between the Safety in Mines Research Board of Great Britain and the Bureau of Mines, United States Department of the Interior. Under this cooperative arrangement, begun in 1924, the exchange of personnel and data permitted intensive investigation of specific problems dealing with the prevention or abatement of accidents in mines. The determination of constants such as the limits of flammability and explosibility of gases and dusts encountered in mines and the mineral industries was part of the cooperative program.

Dr. H. F. Coward, of Sheffield, England, was detailed by the British Safety in Mines Research Board in April 1925 to the experiment station of the Bureau of Mines at Pittsburgh, Pa., to make a cooperative study of certain chemical and physical factors connected with the initiation and propagation of flame in different gases under various conditions. G. W. Jones, of the Bureau of Mines, was detailed to work in association with Dr. Coward.

A knowledge of the limits of flammability of methane and of the distillation products of coal in air and in partly vitiated atmosphere is of fundamental importance in the study and prevention of mine explosions. Likewise, a knowledge of the flammable limits of gasoline and benzol vapors, natural and manufactured gas, blast-furnace gas, hydrogen, acetylene, and many other gases is of equal importance in preventing gas explosions and fires in the metallurgical, petroleum, gas-manufacturing, and related industries.

Substances that a short time ago were found infrequently, even in the laboratory, are being used on a large scale as anesthetics, insecticides, solvents for lacquers and resins, etc., and some of them form dangerously explosive mixtures with air. The importance of such data is shown by the increasingly frequent inquiries received by the Bureau of Mines for information on the limits of flammability of various gases and vapors when mixed with air or other "atmosphere." Data on limits are widely scattered in the literature, and many of the figures seem contradictory. In the following pages they have been arranged, coordinated, and critically reviewed. The opportunity has been taken to include a number of results that have not hitherto been published. There are now 155 substances in the summary of flammability limits in air and in oxygen as against 26 in the first edition.

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By

H. F. Coward[2] and G. W. Jones[3]

PART I. DETERMINATION OF LIMITS

DEFINITIONS

A FLAMMABLE mixture of gases, such as methane and air, may be diluted with one of its constituents or with other gases until it is no longer flammable. The dilution limit of flammability, or simply the limit of flammability, is the borderline composition; a slight change in one direction produces a flammable mixture, in the other direction a nonflammable mixture.

There are clearly two limits of flammability, a lower and a higher, for each pair of so-called combustible gases and supporters of combustion. The lower limit corresponds to the minimum amount of combustible gas and the higher or upper limit to the maximum amount of combustible gas capable of conferring flammability on the mixture. For example, for methane-air mixtures these limits under normal conditions are approximately 5 and 14 percent methane, respectively. Mixtures within these limits liberate enough energy on combustion of any one layer to ignite the neighboring layer of unburned gas and are therefore capable of self-propagation of flame; others are not. Mixtures richer than 14 percent methane, however, may burn on contact with external air, for mixtures that contain less than 14 percent methane are formed in the zone where the gases mingle.

The experimental determination of limits of flammability is more difficult than may be expected, as is shown by the contradictory figures reported from time to time. This bulle-tin presents the results of a critical review of all figures published on the limits of flammability of combustible gases and vapors when admixed with air, oxygen, or other "atmosphere." Suspended dusts and liquid mists are not considered, except in one or two instances in which direct comparison can be made with vapors.

CONDITIONS FOR PROPAGATION OF FLAME IN MIXTURES OF GASES

SOURCE OF IGNITION

When a source of heat of sufficient size and intensity is introduced into a weak mixture, some combustion occurs, even when the mixture is incapable of self-propagation of flame. This is often visible as a "cap" of flame, which may be large if the source of heat is ample. The flame cap may be fixed in relative position to the source of ignition, as in a miner's flame lamp burning in a gassy atmosphere, or may become detached from the source and float for a limited distance in a moving atmosphere, or may travel away 2 or 3 feet from an initiating spark or flame in a still atmosphere (*236*).[4] Such flames are not self-propagating, as they are extinguished when the influence of the source of ignition is lost.

When a weak source of ignition is employed, some flammable mixtures, especially those near the limits, may not inflame. The source of ignition is not strong enough to be satisfactory for the test.

As the test concerns the capability of the mixture to propagate flame, not the capacity of the source of energy to initiate flame, it is

[4] Italicized numbers in parentheses refer to Bibliography at end of this bulletin.

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axiomatic that the limits are unaffected by variations in the nature and strength of the source of ignition. When statements are made that limits vary according to the means of ignition, it is clear that the observers used either such strong sources of ignition that the caps of flame gave the appearance of general inflammation or such weak sources that flame was not started in mixtures which were, in fact, flammable. Under these conditions they were determining the limits of ignitibility by the particular sources of ignition they used, not the limits of flammability of the mixture itself (63, 227).

DIRECTION OF FLAME PROPAGATION

When a source of ignition, such as an electric spark or a flame, is introduced into a flammable mixture, flame tends to travel away from the source in all directions. In a very large volume of mixture the form of the zone of combustion would be a spherical shell of increasing radius were it not that the hot expanded products of combustion tend to rise and hence to introduce convection currents. Flame cannot travel downward when the upward movement of the gases, due to convection, is faster than the speed of flame in a still mixture, as happens in weak mixtures near the limits of flammability. Hence, near each limit there is a range of mixtures that will propagate flame upward but not downward. These may correctly be termed "flammable mixtures," as it is only necessary to ignite them near their lower confines to observe self-propagating flame traveling to the higher confines. The gentle convection current set up by the flame increases the apparent speed of flame but, as far as is known, does not enable flame to travel when in the absence of convection effects it would not be propagated (63). It seems correct, therefore, to observe upward propagating flames when defining the limits of flammability of gas mixtures; but, for some purposes, it is desirable to know the limits of flammability for propagation of flame in other directions (33). Such limits when determined are included in the experimental results given in this bulletin.

For safety in industrial operations it is generally wisest to consider the limits for upward propagation as the danger line, since these limits are wider than those for horizontal or downward propagation of flame.

DIAMETER OF VESSEL

The propagation of flame depends upon the transfer of energy from the burned to the neighboring unburned gas, and in a limit mixture the amount of energy available for transfer is only just enough to maintain flame propagation; therefore, anything that reduces the available energy will affect the limits. Hence, it is necessary to make observations in vessels wide enough that the effect of cooling by their walls is negligible.

The observed limits of flammability are almost always widened as tube diameter is increased, rapidly at first and more slowly afterward, so that increase of diameter above 5 cm. rarely shows more than a few tenths of 1 percent increase in the range of flammability; many examples of this may be found in the tabulated results in the following pages, but there are a few notable exceptions. For example, while the higher limit (downward or horizontal propagation of flame) of acetylene-air mixtures is much increased by enlarging the diameter of the vessel beyond 5 cm., the higher limits (upward propagation of flame) of hexane and ethylene are much reduced. Moreover, the abnormal "cool flame" in higher-limit acetone-air mixtures appears to be able to travel upward in certain mixtures in a 2.5-cm. tube but not in 5- or 7.5-cm. tubes. With few exceptions, however, the general rule holds.

LENGTH OF VESSEL

When flame travels from the open end of a tube toward the closed end, its speed is uniform over a distance that depends on the composition of the mixture and the dimensions of the tube; the inflammation of one layer of gas repeats the inflammation of any other layer in the "uniform movement" of flame. Sooner or later vibratory movement of the flame may replace the uniform movement; but this is rarely observed in limit mixtures. When it has happened, however, the simple expedient of holding a pad of cotton wool loosely against the open end of the tube has suppressed any tendency to vibration without sensibly hindering maintenance of constant pressure conditions. The flame then travels throughout the tube at uniform speed; and variation in length of the tube, provided it is long enough (say, 4 feet) for the initial impulse of the source of ignition to be dissipated, has no effect on the limits observed therein.

In experiments with closed tubes, however, it is untrue that the length of tube does not affect the results. The longer the tube the smaller must be the pressure attained during propagation of a limit flame, because in longer tubes the gases behind the flame have time to cool more before the flame reaches the end of its journey. Schützenberger (503) showed long ago that the observed limits in closed tubes are affected by the length of tube. In experiments with mixtures of 10 percent hydrogen and 90 percent oxygen he found that there was "a maximum length of column of gas, beyond

which flame is propagated only a short way from the spark, whilst it can be propagated for lesser lengths" (of column of gas). An elaborate experimental study has confirmed and extended these observations (322).

EFFECT OF SMALL CHANGES IN ATMOSPHERIC COMPOSITION

Humidity.—Some gas mixtures are exceedingly difficult to ignite if they have been dried by long-continued contact with phosphorus pentoxide. Such a degree of dryness is peculiar to the laboratory and is not considered in the present review.

Limits have sometimes been determined with roughly dried mixtures in which the partial pressure of water vapor is less than 1 mm., sometimes with mixtures saturated with water vapor at the temperature of the laboratory. The condition of humidity has not always been stated, perhaps because it has been assumed to be negligible. Probably the difference is appreciable for most gases only in exact work. Thus, the lower limit of methane in air, in certain comparative experiments, was found to be 5.24 percent for a mixture dried by calcium chloride and 5.22 percent for one saturated with water vapor at laboratory temperature. These are actual percentages and are equal within experimental error; but, as usually reported from analyses calculated on a dry basis, they appear as 5.24 and 5.33 percent, respectively. For methane, therefore, the true lower limit is not appreciably affected by the replacement of about 2 percent of air by an equal volume of water vapor. The higher limit, however, is reduced by such a replacement, because the oxygen content, which is less than the amount required to burn the methane completely, is thereby reduced. For example, the corresponding higher limits for methane in dry and in saturated air are 14.02 and 13.54 percent, respectively; expressed on a dry basis (as reported analytically) these figures become 14.02 and 13.80 percent, respectively (69).

Carbon monoxide shows greater differences than methane. The lower limit of carbon monoxide in air saturated with water vapor at laboratory temperature was 13.1 percent for upward propagation of flame in a 2-inch tube; if the gases were dried by passage over calcium chloride, the lower limit became 15.9 percent (70). Such a large difference is exceptional, perhaps unique, as moderate drying of carbon monoxide-air mixtures affects their ignition temperatures and flame speeds more than it affects these properties of any other gas hitherto examined.

Oxygen Content.—The lower limit of methane-air mixtures and of some, probably all, other mixtures is not appreciably affected by small changes in the oxygen content of the air. The higher limit is noticeably depressed by a small reduction in oxygen content, because a correspondingly smaller amount of the combustible gas can burn. Thus, reduction of the oxygen content of the air from 20.9 to 20.6 percent depressed the higher limit of methane about 0.3 percent. (See fig. 20.)

PRESSURE

The normal variations of atmospheric pressure do not appreciably affect the limits of flammability, as has been shown both by direct observation and by deduction from the course of curves showing the variation of limits over much wider variations of pressure than those of the atmosphere (14, 17, 95, 154, 225, 235, 309).

The effect of larger variations in pressure is neither simple nor uniform but is specific for each flammable mixture. So far as is known, reduction in pressure below 760 mm. generally narrows the range of flammability by raising the lower limit and decreasing the higher limit. This change is often imperceptible for the first few hundred millimeters' fall in pressure below atmospheric, but thereafter the effect increases until at a suitably low pressure the limits coincide; below this point no mixture can propagate flame (65, 171a, 180).

The limiting pressure is somewhat difficult to find, because often it is so low that the difficulty of insuring a powerful enough source of ignition has not certainly been overcome. For example, in electrolytic gas a flame that filled a 570-cc. globe has been produced at 5 mm. pressure, and with the same mixture flame traveled through a cylinder 2 meters long at 8 mm. pressure (66). At such pressures the electric discharge used to test the flammability was diffuse and if made stronger might have produced self-propagating flames at still lower pressures. For this reason the rate at which the lower- and higher-limit curves approach one another as the pressure is decreased will appear to depend on the strength of the source of ignition, unless the source is carefully made strong enough to insure ignition and the vessel used is large enough for the flame to travel such a distance from the source as will enable observers to see whether the mixture is capable of self-propagation of flame. This has not been done, so the course of limit curves at very low pressures is unknown. In attempting to discover the course of such curves, the difficulty of maintaining constant pressure during the inflammation will have to be surmounted. However, it is almost certain that whatever may be the exact course of the curves they do approach and ultimately meet as the pressure is decreased.

Increase of pressure above that of the atmosphere does not always widen the limits. On the contrary, the range of flammability of some mixtures is narrowed by increase of pressure, so that a mixture that can propagate flame at atmospheric pressure may not be able to do so at higher pressures. For such mixtures the lower limit may pass through a minimum and the higher limit through a maximum at pressures (not necessarily the same) equal to or greater than that of the atmosphere (277, 324). Details are given in the paragraphs on the effect of pressure on the individual mixtures, more especially those of air with hydrogen, carbon monoxide, the simpler paraffin hydrocarbons, natural gas, and ethylene.

Attention may be called to the observations that the range of flammability of hydrogen-air and carbon monoxide-air mixtures (downward propagation of flame) is narrowed at both limits by moderate increases of pressure above atmospheric and that under the same conditions the range of each of the gases of the paraffin series, with air, is narrowed at the lower-limit side (by moderate increase of pressure beyond a certain critical value) but widened at the higher-limit side. It has been suggested that the loss of heat by convection is greater at high pressures than at low, as density differences are greater at high pressures, therefore that the range should be narrowed at both limits when flame is traveling downward. This would explain the results for hydrogen (both limits, moderate pressures), carbon monoxide (both limits, all pressures), and the paraffin gases (low limit only, moderate pressures). Superposed on this effect is another, however. According to the law of mass action, and assuming complete oxidation in one stage, the rate of reaction at constant temperature is greatest in methane-air mixtures when 33.3 percent methane is present. The mass-action effect becomes a more important factor as the pressure is raised and hence tends to raise the higher limit in methane-air mixtures with increase of pressure. A similar explanation may be given for higher-limit curves of the other paraffin hydrocarbons. For hydrogen and carbon monoxide, however, the mass-action law indicates that the 66.7-percent mixture has the greatest rate of reaction at constant temperature. As the higher limit of each of these gases is above 66.7 percent, the effect of mass action would not tend to reverse the effect of convection (277). The more recently discovered rise in the higher limit of hydrogen at pressures from 10 to 220 atmospheres calls for explanation along other lines (14, 17).

The foregoing argument on the influence of convection on the limits of flammability was applied to results of experiments on downward propagation of flame. The argument was supported by the discovery that for horizontal propagation, in which the flames could not be retarded by convection and might even be assisted, the lower limit of methane in air remained unaltered between 760 and 5,000 mm. pressure, and the higher limit was increased even more than for downward propagation (277).

With only one exception known to the writers (104), all measurements of limits at pressures above or below atmospheric have been made in closed vessels, hence the results relate to pressures that increased at an unknown rate and to an unknown amount during the experiment. The rate and amount would vary with the size and shape of the container.

The same criticism applies to experiments in closed vessels when the pressure is initially atmospheric; the results obtained are a function of the length of the vessels used, as this governs, in part, the rate and amount of pressure development (63).

TEMPERATURE

To propagate flame, the layer of unburned gas next to the burning layer must be brought to such a temperature that it will "burst into flame" rapidly. If the unburned gas is already at a temperature above that of the laboratory, less heat has to be supplied from the burning layer; therefore the lower limit should be decreased by increase of initial temperature and the higher limit should be increased. In other words, the range of flammability should be widened at both limits by increase of temperature.

Experiment has shown that, for most mixtures, there is a straight-line relation between the limit of flammability and the initial temperature of the mixture (358). This relation was obscured in earlier experiments by errors due to slow combustion, which changed the composition of the mixture while it was in the heated vessel and before it was tested by sparking. The same error presumably explains those results in which a widening of the range of flammability was not observed.

Ordinary variations of laboratory temperature have no appreciable effect on limits of flammability.

TURBULENCE

Few observations have been made on the effect of turbulence on limits of flammability, but it has been shown that the lower limits of methane and ethane in air are reduced somewhat by a suitable amount of turbulence produced either by a fan or by stream movement of the mixture and that the range of flamma-

bility of ether-air mixtures is somewhat widened by stream movements.

Turbulence caused by fans or by the detonation of explosives affects the lower limit cf natural gas somewhat. (See the paragraphs that deal with these mixtures.)

LIMITS IN AIR COMPARED WITH LIMITS IN OXYGEN

In general, the lower limit cf a gas is nearly the same in oxygen as in air, but very few strictly comparable results are available to show whether small differences exist. The lower limit of methane, observed with central ignition in a globe or with downward propagation of flame in a tube, is rather higher in oxygen than in air (267, 271), presumably because the mean molecular heat of oxygen is higher than that of nitrogen between room temperature and that of a limit flame, say, 1,200° to 1,400° C. For upward or horizontal propagation the lower limit of methane is slightly less in oxygen than in air; the ammonia limit is markedly less (271). The higher limits of all flammable gases are much greater in oxygen than in air; hence the range of flammability is always greater in oxygen.

EFFECT OF CHEMICALLY INERT SUBSTANCES

The addition of increasing amounts of a chemically inert substance to the atmosphere causes the limits of a gas to approach and ultimately to meet. Many examples can be found in the following pages, but the most complete series available is for methane limits, as illustrated in figures 24 and 29. The extinctive efficacies of the five diluents, carbon tetrachloride, carbon dioxide, nitrogen, helium, and argon, decrease in the order given, that is

$$CCl_4 > CO_2 > N_2 > He > A.$$

The experiments giving these results were carried out in tubes of 5 cm. diameter. In tubes of 2.2 cm. diameter the order of the last four diluents, for several combustibles, is (341):

$$CO_2 > He > N_2 > A.$$
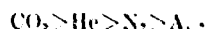
In still narrower tubes, 1.7 and 1.6 cm. diameter, the order is (194, 285):

$$He > CO_2 > N_2 > A.$$

It will be seen that the order $CO_2 > N_2 > A$ is the same in all experiments, but that helium tends to rise in efficacy as the diameter of the tube in which the experiments are made decreases. The effects of carbon tetrachloride, carbon dioxide, water vapor, nitrogen, and argon correspond closely with their specific heats, but the very high thermal conductivity of helium tends to give it an abnormal position

in the series; this effect is enhanced in the narrower tubes because of the greater readiness with which helium conducts heat from the gases to the walls of the tube, thus cooling the flame in this way more than do the other gases named (94).

From curves showing the effect of an inert diluent on the limits of flammable gas in air, it is easy to deduce (1) the minimum percentage of oxygen that will support inflammation of the mixture or the maximum permissible if it is desired to make a nonflammable mixture, (2) the minimum percentage of inert diluent that must be mixed with a combustible gas if it is desired that none of its possible mixtures with air can propagate flame. Many examples are given later in the text. A graphical method of deducing such results has been put forward by Burgoyne and Williams-Leir (39), with tabulated results. From these, with the additional knowledge of the limits in air, it is possible to make a more or less accurate reconstruction of the flammability-limit curves.

MIXTURES OF FLAMMABLE GASES AND VAPORS

A simple formula, of additive character, was advanced by Le Chatelier (218) to connect the lower limits of two gases with the lower limit of any mixture of them. It is

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} = 1,$$

in which N_1 and N_2 are the lower limits in air for each combustible gas separately and n_1 and n_2 are the percentages of each gas in any lower-limit mixture of the two in air.

The formula indicates that, for example, a mixture of air, carbon monoxide, and hydrogen, which contains one-quarter of the amount of carbon monoxide and three-quarters of the amount of hydrogen necessary to form a lower-limit mixture, will be a lower-limit mixture. If the formula is true, the lower limits of flammability form a series of flammability equivalents for the individual gases of a mixture (64).

The formula also indicates that lower-limit mixtures, if mixed in any proportions, give rise to mixtures that are also at their lower limits; or, vice versa, the formula may be deduced from the latter statement as a postulate (64).

The formula may be generalized to apply to any number of combustible gases, thus:

$$\frac{n_1}{N_1} + \frac{n_2}{N_2} + \frac{n_3}{N_3} + \ldots = 1,$$

and, so far as it expresses experimental results truly, may be applied to higher-limit mixtures, with the appropriate rewording of the definition of $N_1 \ldots$ and $n_1 \ldots$.

A small algebraic transformation gives a more useful formula for calculating the limits of any mixture of combustible gases that obeys it (64), as follows:

$$L=\frac{100}{\frac{p_1}{N_1}+\frac{p_2}{N_2}+\frac{p_3}{N_3}+\cdots}.$$

in which L is the limit of the mixture of combustible gases and p_1, p_2, p_3 . . . are the proportions of each combustible gas present in the original mixture, free from air and inert gases, so that

$$p_1+p_2+p_3+\cdots=100.$$

An example of the use of the formula will make its application clear: The lower limit of a "natural gas" of the composition

	Percent	
Methane	80	(lower limit, 5.3)
Ethane	15	(lower limit, 3.22)
Propane	4	(lower limit, 2.37)
Butane	1	(lower limit, 1.86)

is given by

$$L=\frac{100}{\frac{80}{5.3}+\frac{15}{3.22}+\frac{4}{2.37}+\frac{1}{1.86}}=4.55 \text{ percent.}$$

The accuracy of the formula has been tested carefully for many mixtures. The results are discussed separately in the appropriate sections later. In general, it may be said that, while the formula is often correct or very nearly so, there are some marked exceptions. It seems that the limits (lower and higher) of mixtures of hydrogen, carbon monoxide, and methane, taken two at a time or all together, and of water gas and coal gas may be calculated with approximate accuracy (64). The same is true for mixtures of the simpler paraffin hydrocarbons, including "natural gas" (74). Sometimes, however, the differences between calculated and observed values are very large; for examples, see figures 56 and 57. Many of the greater discrepancies are found with upward-propagating flames, especially when one of the constituents is a vapor, such as ether or acetone, capable of giving rise to the phenomenon known as a "cool flame" (355). Le Chatelier's law is useful when its applicability has been proved, but it should not be applied indiscriminately.

Limits of Industrial Mixtures Containing Hydrogen, Carbon Monoxide, Methane, Nitrogen, Carbon Dioxide, and Perhaps Air.—An extension of the law to apply to other atmospheres than air (95, 271, 272) is that, when limit mixtures are mixed, the result is a limit mixture, provided that all constituent mixtures are of the same type; that is, all are lower-limit mixtures or all are higher-limit mixtures. This law holds, for example, for methane in a range of oxygen-nitrogen mixtures and in air-carbon dioxide,

air-argon, and air-helium mixtures, except near the point at which lower and higher limits meet, where the proportion of inert gas is large. It holds also for mixtures of hydrogen, methane, and carbon monoxide, in a wide range of mixtures of air, nitrogen, and carbon dioxide, and may therefore be used to calculate the limits of flammability of mine-fire gas mixtures and of the atmospheres after a mine explosion, of blast-furnace gas, of automobile-exhaust gas, and of the gases from solid explosives (133, 367).

A brief account of the method of calculating limits of complex industrial gases, such as those just mentioned, follows. Greater detail will be found in the original account (133).

The chief gases in these mixtures are hydrogen, carbon monoxide, methane, nitrogen, carbon dioxide, and oxygen. The procedure is as follows:

1. The composition of the mixture is first recalculated on an air-free basis; the amount of each gas is expressed as a percentage of the total air-free mixture.

2. A somewhat arbitrary dissection of the air-free mixture is made into simpler mixtures, each of which contains only one flammable gas and part or all of the nitrogen or carbon dioxide.

3. The limits of each mixture thus dissected are read from tables or curves. (See figs. 1 and 2.)

4. The limits of the air-free mixture are calculated from the figures for the dissected mixtures obtained in (3), by means of the equation:

$$L=\frac{100}{\frac{p_1}{N_1}+\frac{p_2}{N_2}+\frac{p_3}{N_3}+\cdots},$$

where p_1, p_2, p_3 . . . are the proportions of the dissected mixtures, in percentages, and N_1, N_2, and N_3 . . . are their respective limits.

5. From the limits of the air-free complex mixture thus obtained the limits of the original complex mixture are deduced.

The following is an example of the calculation applied to a mine-fire atmosphere. It contained:

Constituent	Per-cent	Air-free, percent	Constituent	Per-cent	Air-free, percent
Carbon dioxide	14.4	15.9	Methane	3.3	3.8
Oxygen	2.8	.6	Hydrogen	4.9	5.7
Carbon monoxide	4.3	5.0	Nitrogen	70.9	69.6

1. The composition on an air-free basis, also given above, is found thus:

The amount of air in the mixture is $2.8 \times 100/20.9=13.4$ percent. The air-free mixture is therefore 86.6 percent of the whole. When the original amounts of carbon dioxide, carbon monoxide, methane, and hydrogen are divided
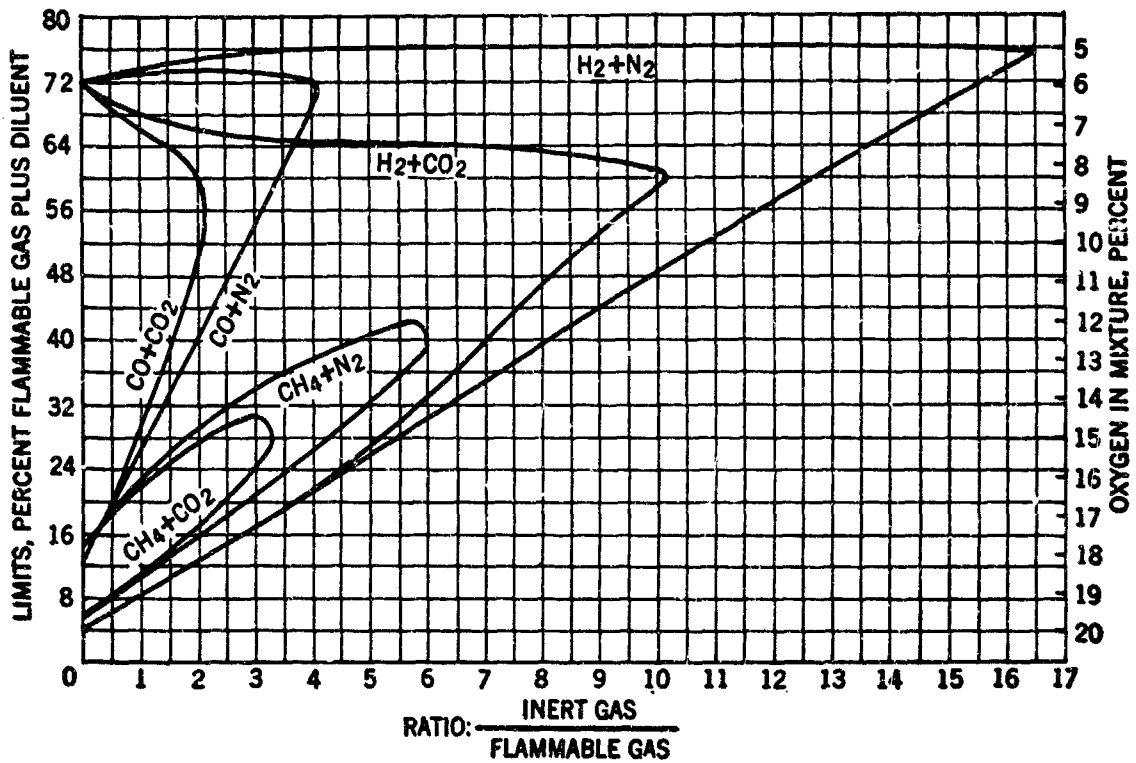
FIGURE 1.—Limits of Flammability of Hydrogen, Carbon Monoxide, and Methane Containing Various Amounts of Carbon Dioxide and Nitrogen.
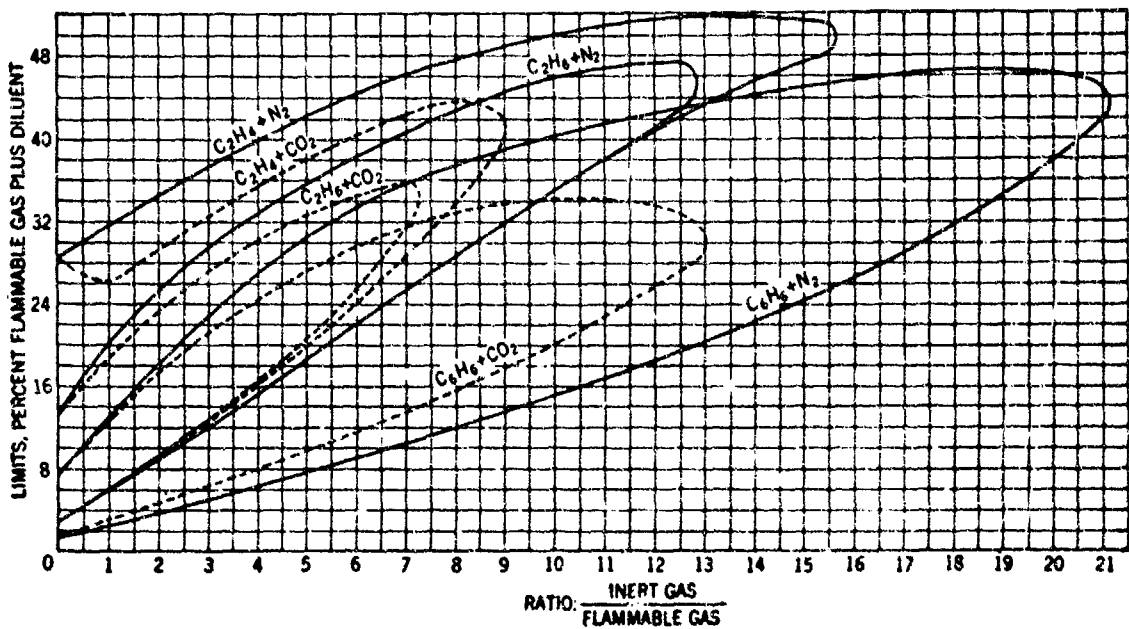
FIGURE 2.—Limits of Flammability of Ethane, Ethylene, and Benzene Containing Various Amounts of Carbon Dioxide and Nitrogen.

by 86.6 and multiplied by 100, the "air-free" percentages are obtained. The nitrogen figure is the difference between 100 and the sum of these percentages.

2. The flammable gases are paired off with the inert gases separately to give a series of dissected mixtures, as shown in the following table.

Combustible	Percent	CO_2, percent	N_2, percent	Total percent	Ratio of inert to combustible	Limits from fig. 1	
						Lower	Higher
CO	5.0		17.5	22.5	3.5	61	73.0
CH₄	3.8		20.9	24.7	5.5	36	41.5
H₂	5.7 {3.0 / 2.7	15.9	31.2	34.2 / 18.6	10.4 / 5.9	50 / 32	76.0 / 64.0
Total	14.5	15.9	69.6	100.0			

Some discrimination is needed to choose appropriate quantities, but a fair latitude of choice is usually available.

3. The limits of the dissected mixtures, from figure 1, are shown in the last two columns above. For example, the first mixture contains 5.0 percent of carbon monoxide and 17.5 percent of nitrogen; the ratio between its nitrogen and carbon monoxide is 17.5:5.0=3.5; and the limits from the curve for carbon monoxide-nitrogen mixtures are 61 percent (lower) and 73 percent (higher).

4. The values in the last two columns and in the column "Total percent," substituted in the equation, give the two limits of the air-free complex mixture, calculated to 0.5 percent:

$$\text{Lower limit} = \frac{100}{\frac{22.5}{61} + \frac{24.7}{36} + \frac{34.2}{50} + \frac{18.6}{32}} = 43 \text{ percent,}$$

$$\text{Higher limit} = \frac{100}{\frac{22.5}{73} + \frac{24.7}{41.5} + \frac{34.2}{76} + \frac{18.6}{64}} = 61 \text{ percent.}$$

The range of flammability of the air-free complex mixture is therefore 43 to 61 percent.

5. As the air-free mixture is 86.6 percent of the whole, the limits, in air, of the mine-fire atmosphere are 43×100÷86.6, and 61×100÷86.6, or 50 and 70 percent, respectively.

The novice's difficulty with such calculations is in stage 2, where an appropriate amount of inert gas has to be chosen to pair with each combustible gas in turn. The ratio of inert to flammable gas must not be so high that the mixture falls outside the extreme right of the corresponding curve in figure 1. A little practice will soon overcome this difficulty.

It need only be added that, if the amount of inert gas is so great that a complete series of flammable mixtures cannot be dissected, the air-free mixture is not flammable. Moreover, the air-free mixture may be flammable, but when its limits are multiplied by the appro-

priate factor in the final stage of the calculation the result may be greater than 100 for each limit; the original mixture is then incapable of forming an explosive mixture with air because it contains too much air already. Finally, if the lower limit of the original mixture is less than 100 and the higher limit greater than 100, the mixture is flammable per se and would explode if a source of ignition were present.

About 20 examples, which cover a wide range of industrial gases, have been tested (133) by experiment. The calculated and observed limits agree within 2 or 3 percent, excepting one higher-limit figure for a mixture that contained an unusually large amount (nearly 24 percent) of carbon dioxide.

Extension of Mixture Law.—The combustible gases covered by the examples just given are hydrogen, carbon monoxide, and methane. The necessary data for the limits of ethane, ethylene, and benzene are available (fig. 2), and these three gases have been included in calculations of the limits of complex industrial combustibles, such as coke-oven gas, coal gas, carbureted water gas, oil gas, and producer gas (136).

Safety of Industrial Mixtures of Gases.—If a complex mixture of combustible and incombustible gases, such as any of those just discussed, is flammable per se or is capable of forming flammable mixtures with air, the minimum amount of incombustible gas that will render it nonflammable and also incapable of forming a flammable mixture with air can be calculated by a small (and justifiable) extension of Le Chatelier's law. This procedure also gives the maximum percentage of oxygen below which all possible mixtures are nonflammable [(62), elaborated in (2)]. A somewhat elaborate graphic method of ascertaining the flammability of triple mixtures of combustible gases has been given (15).

The purging of gas-manufacturing plants and distribution mains by the use of carbon dioxide

or automobile exhaust gas or specially prepared inert mixtures of low oxygen content can be controlled by applying similarly deduced data. A full description is given in reference *329*. Data for purging with steam are given in reference *368*.

SUPPRESSION OF FLAMMABILITY

A flammable mixture may be rendered non-flammable by (*a*) a suitable increase in the amount of either constituent, (*b*) the addition of a suitable amount of chemically inert substance, and (*c*) the addition of a flammable substance in sufficient amount to exceed the higher limit of the resultant mixture. It has been suggested (*129*) that the last-named may be advantageous and technically feasible in certain circumstances when the added flammable substance has a low higher limit of flammability. For example, the mixture of hydrogen and air containing just enough oxygen to burn the hydrogen completely (29.5 percent hydrogen) becomes nonflammable in final mixtures containing 86 percent of air, or 65 percent of hydrogen, or 67 percent of nitrogen, or 10 percent of methane.

CHOICE OF EXPERIMENTAL CONDITIONS

In the light of the preceding discussion, it seems that limits of flammability are physico-chemical constants (at defined temperatures and pressures) of gases and vapors that can be determined when observations are made with quiescent mixtures in vessels of large enough dimensions, with ignition from below (and, if desired, at other points) and with maintenance of constant pressure during the experiment. A somewhat wide experience has shown that, if observations are made in a vertical tube 2 inches in diameter and 4 to 6 feet in height, the results are nearly but not quite, the same as those obtained in much larger apparatus. Limits observed in smaller apparatus—for example, tubes of 1 inch diameter or less—are usually significantly narrower. Results obtained in small, closed tubes often differ so much from normal results, and even from one another, that they may be very misleading.

Mixtures for test are made in gasholders over water, mercury, or other suitable liquid before introduction into the test apparatus; or they are made in the apparatus itself by introducing the components separately and using some mixing device; or they are made by supplying constant metered streams of the components via some suitable mixing device.

Effective ignition usually can be obtained equally well by passing an electric spark from an induction coil (say, from "2-inch" to "12-inch" as convenient) across a gap several millimeters long or by drawing the flame of a small spirit lamp or a jet of burning hydrogen across an aperture in the observation vessel. This aperture is conveniently made at the moment preceding ignition by gently sliding away a ground-glass plate that previously had sealed the vessel. When gases of small solubility are tested, a water seal may be used for this purpose. For a few gases a small tuft of guncotton fired by a spark or heated platinum wire is a more certain means of ignition (*353*, *171a*); for a few others, an electric spark succeeds in firing the mixture when a flame fails (*132*). Ignition attempted by an electrically heated wire may not always be reliable with mixtures near the limits.

Bureau of Mines Apparatus.—An apparatus used for many of the determinations made in the Bureau of Mines laboratory and recorded in the following pages is illustrated in figure 3. It is specially designed for determining limits of vapors of liquids that are sufficiently volatile at laboratory temperatures; it can be simplified for gases, but must be elaborated for the vapors of less-volatile liquids.

In figure 3, *a* is the glass tube in which the mixture is tested. Its lower end is closed by a lightly lubricated ground-glass plate *b*, sealed with mercury *c*. It is evacuated by a pump through the tube *j*. The vapor under test is drawn from its liquid in the container *p*, in amount measured by the manometer *k*. Air or other "atmosphere" is then admitted through the drying tube *q* until atmospheric pressure is reached. The air and vapor are then thoroughly mixed by circulation, by suitably raising and lowering the mercury vessel *g* repeatedly for 10 to 30 minutes, depending upon the density of the added combustible vapor. The mercury seal is then removed, the glass plate *b* is slid off the tube, and the flammability is tested almost at the same moment by sparking at *y* or by passing a small flame across the open end of the tube.

Special Conditions.—An examination of the effects of temperature on limits of flammability requires special arrangements for heating (or cooling) the test vessel. These are not difficult to provide. To examine the effect of pressure is, however, much more difficult because of the problem of avoiding large increases of pressure during (and as a result of) the inflammation. A few experiments have, however, been made with the "open" end of the test vessel in connection with a very much larger vessel full of air at the same pressure as that of the mixture under test (*104*). Most of our information about pressure effects on limits relates only to the pressure of the mixture before inflammation.

The limits of turbulent mixtures have us-
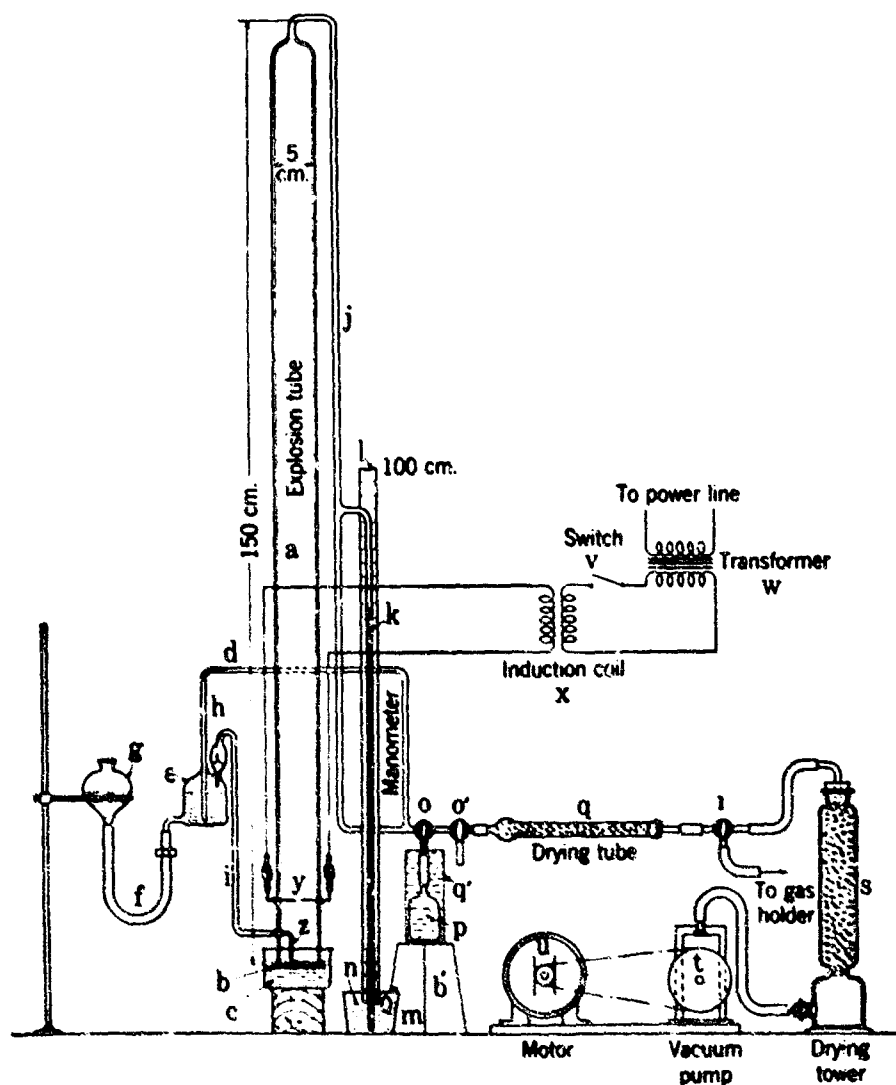
Figure 3.—Apparatus for Determining Limits of Flammability of Gases and Vapors.

ually been determined in small vessels fitted with fans, and the criterion of continued propagation of flame has not been applied, although for testing the effect of turbulence due to the detonation of solid explosives short sections of a cylindrical metal gallery of 6.3 feet diameter have been used.

Stationary Flame in a Flowing Mixture.— Quite recently (286) an apparatus has been devised from which a cylindrical column of gaseous mixture rises into the air in a uniform stream, "jacketed" by a layer of nitrogen which helps to maintain the strict uniformity of motion of the mixture. The success of this device is shown by the fact that flat, stationary, horizontal flames have been maintained in mixtures of composition slightly below the lower limits determined in tubes. Only two figures of limits determined by means of this device are yet available (see under Propane and Butane).

PART II. SOME THEORETICAL CONSIDERATIONS

Nobody has succeeded in calculating either a lower or a higher limit of flammability of any mixture from more fundamental physicochemical data. In general terms, the problem is to express quantitatively the fact that there comes a point in the progressive dilution of a flammable mixture when the production of energy (including that of atoms and radicals) is no longer sufficient to inflame a neighboring layer of unburned mixture.

Some attempts already made to relate limits of flammability to simpler data may be mentioned. Long ago Humphry Davy (78) ascribed to its greater heat capacity the superior effect of carbon dioxide in rendering methane-air mixtures nonflammable; this conclusion has frequently been supported by observations with other flammable mixtures. Regnault and Reiset (292) drew attention to the different ability of hydrogen and oxygen to render electrolytic gas nonflammable; they ascribed it to the different mobilities of these gases or to their different thermal conductivities. As these gases are not chemically inactive toward the constituents of electrolytic gas, chemical effects may play a part. More recently, some comparative experiments with mixtures of methane and atmospheres composed of air and equal volumes of either argon or helium have proved that, when heats of reaction, rates of reaction, and specific heats are equal there is still a large difference in the limits in the argon and the helium mixtures. This difference is ascribed to the different thermal conductivities of the mixtures (69).

Bunsen (26, 27) attempted to calculate ignition temperatures of gas mixtures from their limits of flammability, with the aid of heats of reaction and specific heats. He assumed that the heat produced by the combustion of one layer (already heated, before burning, to its ignition temperature) was transmitted to the neighboring unburned layer, which was inflamed if the heat thus transmitted sufficed to raise it to its ignition temperature. The reverse procedure—calculating dilution limits from the ignition temperatures determined independently—has often been attempted, but the results show only that there is no simple relation between limits and ignition temperatures. For example, as shown in the table below (94), (1) in the series of normal paraffin hydrocarbons the ignition temperature falls rapidly while the calculated flame temperature of the limit mixture rises, (2) there is a barely measurable difference between the lower limits (and flame temperatures) of n- and iso-octane, but a very large difference between their ignition temperatures.

Hydrocarbon	Lower limit, percent by volume	Flame temperature of limit mixture, ° C.	Ignition temperature of hydrocarbon, ° C.
Methane	5.26	1,255	650
n-Butane	1.93	1,445	490
n-Pentane	1.62	1,485	470
n-Hexane	1.46	1,568	273
n-Heptane	1.26	1,509	255
n-Octane	1.12	1,575	245
Iso-octane	1.15	1,606	530

The heat of combustion of a limit mixture of most gases and vapors is enough to raise an equal volume of the unburned mixture to a temperature far higher than its ignition temperature, as usually determined, but probably not as high as the temperature necessary for inflammation within the very small fraction of a second necessary to insure propagation of flame at the observed rates in limit mixtures. This, and other considerations, have led Egerton and Powling (94) to the conclusion that continued propagation of flame depends upon the temperature of the flame being sufficient to maintain a certain boundary flame temperature which provides a certain concentration of active radicals in the boundary region; and that inflammation is produced in the unburned gas mainly by the radicals derived from the flame, that is, only indirectly by the heat of the flame, not directly by heat transference from flame to unburned gas.

The lower-limit mixture of hydrogen in air produces far too little heat to raise the mixture to its ignition temperature, yet flame will travel upward through the limit mixture indefinitely (65). An explanation of this has been given by F. Goldmann (115) at P. Harteck's suggestion. The flame in the limit mixture rises as a luminous ball or balls, consuming only part of the hydrogen. As the hydrogen is consumed, fresh hydrogen diffuses into the flame more rapidly than the other gases; therefore the mixture that is burning is not the same as that in the rest of the containing vessel. This explanation is ren-

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dered highly probable by the observation that particles of finely divided platinum or palladium may be maintained red hot by suspension in a mixture of 4 percent hydrogen and air. Combustion of the mixture produces a temperature of less than 350° C., but the high rate of diffusion of the hydrogen enables a far higher temperature to be maintained at the metallic surface.

Although this explanation of the mechanism of flame propagation in hydrogen-air mixtures is entirely acceptable, it seems undesirable, and possibly dangerous, to accept Goldmann's conclusion that the true limits of flammability are those for downward propagation of flame. If so, a 6-percent hydrogen-air mixture and a 5.6-percent methane-air mixture would be described as nonflammable. Both these mixtures propagate flame upward indefinitely and if ignited near the floor of a closed room would produce pressures of the order of 1 and 4 atmospheres, respectively, and mean temperatures of about 350° and 1,200° C. Such conditions would burst windows and burn men. It is inconceivable that anyone who has seen a 5.6-percent methane-air flame traveling up a long tube would term this mixture nonflammable, although it fails to propagate flame downward.

Mallard (232) and others (20) have attempted to deduce limits of flammability from curves showing the speed of propagation of flame, for example, in a series of mixtures of methane and air. By extrapolating to zero speed they thought to find the compositions of the limit mixtures, but in a limit mixture the speed of flame is by no means zero.

A few regularities, set forth in the following paragraphs, have been discovered; occasionally they may give a useful indication of limits which have not been experimentally determined.

1. Le Chatelier and Boudouard (221, 222) determined the lower limits of some 31 gases and vapors for downward propagation of flame. With the exception of hydrogen and carbon disulfide, which gave low figures, the heats of combustion lay between 9 and 13 large calories per unit volume (23.5 liters at 15° C.) of the limit mixture; for most of them, the range was 12 to 13 large calories.

2. Burgess and Wheeler (32) found that, for the first five members of the paraffin series of hydrocarbons, the calorific values of the lower-limit mixtures (propagation of flame throughout a globe) were nearly equal. The agreement is not so good for limits for upward propagation of flame for these hydrocarbons (74), but a smooth curve can be drawn to represent the relation between the calorific values of the first eight members of the paraffin series and their lower limits (24).

3. White (353) found approximately constant calorific values for 11 of 12 volatile solvents, for propagation of flame upward or downward in lower-limit mixtures or downward in higher-limit mixtures; the values were different for different directions of propagation of flame. Carbon disulfide was the exception. For the others, the products of combustion were similar (nitrogen, carbon dioxide, water vapor, etc.), and the temperatures attained were approximately equal. Hence, the effective ignition temperature for propagation of flame in these mixtures seems to be approximately constant for the same direction of propagation of flame. The observed ignition temperatures of these vapors are much lower, presumably because, in their determination, a much longer time is available for ignition than is available when flame is self-propagating through a mixture. The effective ignition temperature for downward propagation for the 11 solvents and for the first 5 paraffins and for ethylene, propylene, butylene, and carbon monoxide is about 1,400° C., uncorrected for radiation losses. The figures are much less (356) for hydrogen, hydrogen sulfide, and acetylene.

When the initial temperature of the mixture was increased several hundred degrees (310, 358) the ranges were widened and therefore the heat of combustion at each limit was less, but the two factors usually balanced each other so that the flame temperature of the limit mixture remained constant. This was true for the lower limits of methane, ethylene, acetylene, and pentane and for the higher limits of hydrogen and carbon monoxide. The lower-limit temperatures of hydrogen rose nearly 100°, and those of carbon monoxide fell nearly 100° as the initial temperature of the mixture was increased.

A straight-line relationship between temperature and limits (lower and higher) has also been indicated for several other compounds (3).

Although the calorific values of lower-limit mixtures of chemically closely related compounds are often nearly equal, this rule does not apply generally, as is shown by the following selected samples (134).

Combustible	Net heat of combustion, kg-cal per mole	Lower limit of flammability, percent	Calorific value of lower limit mixture
Hydrogen	57.8	4.0	241
Carbon disulfide	246.6	1.25	308
Hydrogen sulfide	122.5	4.3	527
Acetylene	301.7	2.5	754
Ethylene oxide	281.0	3.0	843
Ethylene	316.9	2.75	855
Methane	191.7	5.0	958
Methyl alcohol	149.8	6.72	1,007
Methyl acetate	349.4	3.15	1,101
Methyl chloride	173.7	8.25	1,398
Methyl bromide	172.5	13.5	2,342

4. The cool flame of ether, which is produced and maintained at a much lower temperature than that required to produce the normal flame, is propagated by a range of overrich mixtures which in some circumstances is separate from the range of mixtures that propagate the normal flame (353). The effects of pressure on ignition temperatures and limits of flammability for the two types of flame are similar and in general support the view that the limits for the normal flame, at least, are governed by the thermal properties of the mixtures. The propagation of the cool flame may depend upon a chain reaction (331).

5. Le Chatelier's law, expressing the limits of mixed flammable gases and vapors in terms of the limits of the individual gases and vapors, is fairly accurate for many mixtures but inaccurate for others.

Nagai has offered an explanation for certain deviations from Le Chatelier's law (249). He assumes that, if two gases individually have the same calculated temperature for their limit-mixture flames, which he calls the theoretical flame-propagation temperature (TFPT), the mixtures of these gases will obey the law. If, however, the TFPT's are not equal, the mixed gases will not obey the law. The gas of higher TFPT does not play the part suggested by Le Chatelier's law until the amount of the other gas is increased in lower-limit mixtures or decreased in higher-limit mixtures. Over a greater or smaller middle range of composition the limit mixtures of some pairs of gases have constant TFPT's, therefore these mixtures obey the law over that range.

Mixtures of hydrogen and ethyl bromide (311) support Nagai's argument. Figure 4 shows the lower and higher limits of mixtures of hydrogen and ethyl bromide; for example, one higher-limit mixture contains about 41 percent hydrogen and 2 percent ethyl bromide; the rest of the mixture is air. If the whole range of these mixtures followed Le Chatelier's law, then the straight line joining the lower or higher limit for hydrogen with the corresponding (undetermined) limit for ethyl bromide would give the corresponding limits for all mixtures of these gases. The theoretical flame-propagation temperature of hydrogen is presumably less than that of ethyl bromide; hence, the addition of the first 1 percent of ethyl bromide to the higher-limit hydrogen mixture necessitates a rapid fall in the hydrogen present in order that the flame temperature shall approach that of ethyl bromide. With 1 to 5 percent of ethyl bromide the limits fall on a straight line, as required by Le Chatelier's
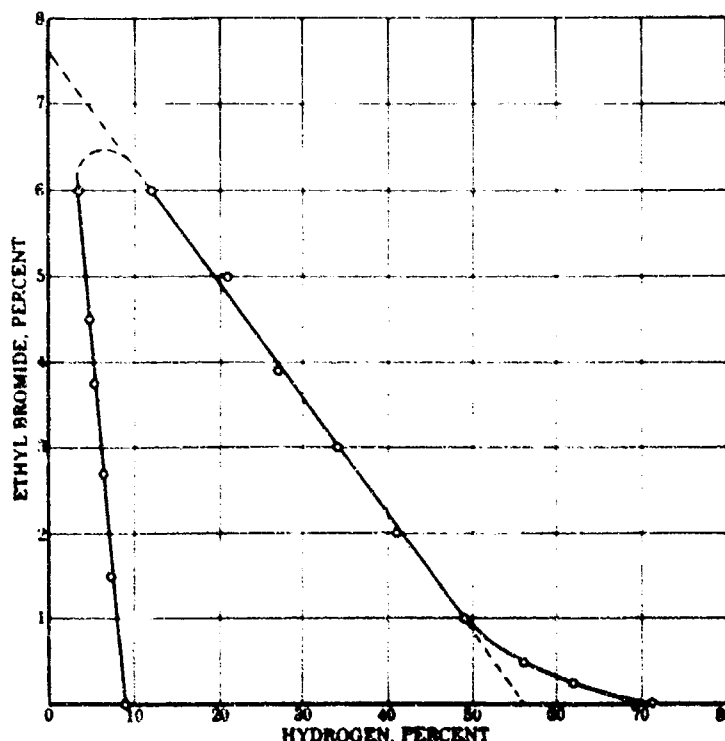
FIGURE 4.--Limits of Flammability of Mixtures of Hydrogen and Ethyl Bromide in Air.

law, because the flame temperatures are equal. Extrapolation of this line cuts the X axis at $X=56$. The TFPT of the mixtures is therefore equal to that of a 56-percent hydrogen-air mixture, which can be calculated. Moreover, the position of any point on the straight part of the higher-limit curve can be calculated on the assumption that the effective limit of hydrogen is 56 percent and that of ethyl bromide 7.6 percent.

Although Nagai has adduced many instances of pairs of gases or vapors that appear to support his views (*246, 247, 250, 252, 311, 314, 315, 316*), others do not. For example, mixtures of hydrogen and methane follow the law of Le Chatelier fairly well, but their TFPT's are far apart. Moreover, mixtures of hydrogen sulfide and hydrogen (fig. 56) and of hydrogen sulfide and methane (fig. 57) present such results as cannot be interpreted by Nagai's ideas.

Another purely empirical relationship between lower and higher limits of hydrocarbons and some of their derivatives has been advanced by M. Aubert (*3*), for downward propagation of flame. The agreement between calculated and observed values is less satisfactory for the simpler compounds than for the more complex and breaks down with acetylene.

6. W. P. Jorissen (*191*) and J. van Heiningen (*342*) of the Leiden school have shown by several examples that the means of the lower and higher limits of two gases in the presence of increasing amounts of an inert third gas have a linear relationship. They correlate these observations with reaction rates based on the law of mass action. The means of the lower and higher limits of two gases have in some, but not all, instances a linear relationship to the pressure (*90*). J. J. Valkenburg has developed this argument further (*336*).

It is apparent that the theoretical treatment of limits of flammability is meager and mainly qualitative; it is bound up with the unsolved problem of the theory of flame propagation in general.

PART III. LIMITS OF INDIVIDUAL GASES AND VAPORS

In accordance with the preceding argument the results collected for individual gases are arranged as follows:

(1) The results of experiments on propagation of flame upward in large volumes of quiescent gas which are at atmospheric pressure during the passage of the flame.

(2) The results for other directions of propagation in similar circumstances.

(3) The results observed in smaller vessels open at one end (so that the pressure is constant during the experiment) or totally closed (so that pressure varies at a rate and to an extent which depends on the dimensions of the vessel used).

The first results may be considered the limits of flammability of the components named, a physicochemical property independent of external conditions, at atmospheric temperature and pressure; the second are the limits under restricting conditions of direction of propagation; the third are the limits under still more restricted conditions, such as the dimensions of the vessel used for observation.

HYDROGEN

HYDROGEN IN AIR

Flames in mixtures of hydrogen and air are exceedingly pale; the flame in a limit mixture is almost or quite invisible, even in a completely darkened room. Ignition by a "fat" electric spark gives rise to a very pale flame, but a "thin" blue spark gives an invisible flame. Proof that an invisible flame has traveled to the top of a vertical tube may be obtained by admitting a small quantity of pure hydrogen to the top of the tube a second or so before the flame is expected to arrive there. If the flame reaches the rich mixture a sharp explosion is observed. Analysis of a limit mixture after the passage of a flame would not prove whether the flame had traveled throughout the length of the tube, for the flames in weak mixtures burn only a fraction of the hydrogen in the tube.

When a spark was passed near the lower confines of a weak hydrogen-air mixture standing over water in a vessel 6 feet high and 12 inches square in section the following observations were made:

4.0 percent hydrogen.—A vortex ring of flame was seen just above the spark gap; it rose, expanded for about 16 inches, then broke and disappeared.

4.2 percent hydrogen.—A similar ring of flame was formed. On breaking, it resolved itself into an exceedingly faint cloud or collection of small balls of flame, which traveled steadily to the top of the containing vessel—a distance of more than 5 feet.

4.4, 4.6, 4.8, 5.2, and 5.6 percent hydrogen.—In each mixture a vortex ring of flame rose about 16 inches, then broke into segments which subdivided into balls of flame that traveled to the top of the vessel. An increasing fraction of the hydrogen present was burned as the amount of it was increased; the strongest mixture, 5.6 percent hydrogen, showed about 50 percent combustion.

In a longer and narrower tube, 15 feet in length and 2 inches in diameter, no flame was seen with 4.2 percent hydrogen, but with 4.4 percent a globular flame traveled at uniform speed the length of the tube. There seems to be no doubt, therefore, that these flames were self-propagating and capable of traveling indefinitely. They left much unburned gas behind because their lateral speed of propagation was much less than their vertical speed, which was due mainly to convection.

In a wide space, therefore, the lower limit of flammability of hydrogen in air is 4.1 ± 0.1 percent.

The hydrogen was not wholly burned in an upward-propagating flame in a tube 2 inches in diameter until 10 percent was present (63).

With a continued source of ignition, such as a succession of sparks or a small flame burning from a jet, weak mixtures showed a continuous thin thread of flame shooting upward and expanding into a flame cloud. As the hydrogen was consumed the thin flame gradually shortened until it disappeared.

Complete combustion of a layer of the limit mixture, 4.1 percent hydrogen, would heat the products to a temperature of less than 350° C. The ignition temperature of hydrogen in air is about 585° C. An ingenious explanation of this anomaly has been given. (*See* pp. 11 and 12.)

The higher limit of flammability has not been determined in large vessels, but experiments in a wide, short vessel and in a long, narrow vessel have indicated (64) that the higher limit in a large volume is about 74.2 percent hydrogen. A more recent determination in a tube 7 cm. in diameter and 150 cm. in length gave the higher limit as 74.4 percent hydrogen (115).

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The foregoing figures, for both limits, refer to gases saturated with water vapor at room temperature. Some recent experiments with dry gases in a 4-inch-diameter tube, open at its lower end, gave the limits for upward propagation as 4.0 and 75.0 percent (*38*). The analytical figures for the moist-gas limits being 4.1 and 74.2 percent, the actual compositions of the moist limit mixtures would be:

	Lower limit	Higher limit
Hydrogen	4.1 = 4.0%	74.2 = 72.5%
Air	95.9 = 94.0%	25.8 = 25.5%
Water vapor, approx	2.0 = 2.0%	2.0 = 2.0%
	102	102

The actual lower limits of dry and saturated gases at room temperature are therefore equal. The actual higher limit is reduced from 75.0 percent to 72.5 percent by saturation with water vapor, a result that is about what would be expected from the known effects of incombustible gases on the higher limits of hydrogen and other gases. It will be noted, also, that the actual percentage of oxygen in the dry and moist higher-limit mixtures is 5.2 and 5.3 percent, respectively, the difference being due presumably to the heat capacity of the water vapor.

Observations in Smaller Vessels.—Table 1 gives additional results for various directions of propagation of flame.

TABLE 1.—*Limits of flammability of hydrogen in air in smaller vessels*
Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed	4.15	75.0	Half-saturated	*356*
5.3	150	Open	4.19	74.6	Dried	*9*
5.3	150	____do	4.12	71.3	do	*9*
5.3	150	____do	4.17	74.8	do	*9*
5.0	150	Closed	4.15	74.5	Half-saturated	*356*
5.0	180	Open	4.0	72.0	Dried	*133*
4.8	150	____do	4.0	73.8	____do	*38*
4.5	80	Closed	4.1			*56*
4.5	80	____do	3.9			*57*
2.5	150	Open	4.2		Dried	*9*
2.5	150	Closed	4.25	73.0	Half-saturated	*356*
2.5	96	____do	4.1	72.8		*98*
2.2	45	____do	3.9	73.0	Saturated	*27*
1.6	96	____do	4.22	71.2		*98*
.8	96	____do	5.1	67.9		*98*

Horizontal Propagation of Flame

7.5	150	Closed	6.5		Half-saturated	*356*
5.0	150	____do	6.7		do	*356*
2.5	150	____do	7.15		do	*356*
2.5	150	Open	6.2		Saturated	*271*
2.5		____do		71.4		*273*
.9	150	____do	6.7	65.7	Saturated	*276*

Downward Propagation of Flame

21.0	31	Open	9.3		Saturated	*68*
8.0	37	Closed	8.9	68.8	do	*324*
7.5	150	____do	8.8	74.5	Half-saturated	*356*
7.0	150	____do		74.5		*115*
6.2	33	Open	8.5		Saturated	*95*
6.0	120	____do	9.45		Partly dried	*325*
6.0	120	Closed	9.3		do	*325*
6.0	120			68.0	do	*325*
5.3	150	Open	9.0		Dried	*94*

See footnotes at end of table.

TABLE 1.—*Limits of flammability of hydrogen in air in smaller vessels*—Continued

Downward Propagation of Flame—Continued

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
5.0	150	Closed	9.0	74.0	Half-saturated	*356*
5.0	65	Open	8.9	71.2		*311*
4.5	80	Closed	³ 9.6			*56*
4.0	50	___do	8.8		Saturated	*63*
2.5	150	___do	9.4	71.5	Half-saturated	*356*
2.5	150	Open	9.7		Saturated	*271*
2.2		Closed	6.8	69.3		*341*
2.2	45	___do	9.1	73.0		*274*
1.9	40	___do	9.45	66.4	Saturated	*356*
1.9	40	___do	9.45	65.25	___do	*323*
1.6	30	___do	7.7	72.6	Dried	*217*
1.4	20	___do	9.8	63.0	___do	*321*

Propagation in a Spherical Vessel or a Bomb

Capacity, cc:						
Not stated	Closed		9.2		Saturated	*271*
Do	___do		8.5	⁴ 67.5	___do	*82*
1,000	___do		8.7	75.5	___do	*95*
810	___do		5.0	73.5		*349*
350	___do		4.6	70.3	Saturated	*368*
35	___do		9.4	⁴ 64.8	___do	*297*

¹ Walls of tube blackened.
² Walls of tube silvered.
³ At 400 mm. pressure.

⁴ This figure would probably have been increased had a stronger spark been used. a spark strong enough to ignite a lower-limit mixture may be too weak to ignite a higher-limit mixture (84).

In round figures, therefore, the limits of hydrogen in air may be stated as follows for gases saturated with water vapor at laboratory temperature and pressure; the figures for the higher limit, downward propagation, are based on observations in closed tubes in which the mixture was under rapidly varying pressure during the experiment:

Limits of flammability of hydrogen-air mixtures saturated with water vapor

	Limits, percent	
	Lower	Higher
Upward propagation	4.1	74
Horizontal propagation	6.0	
Downward propagation	9.0	74

Influence of Pressure.— Figure 5 shows various results obtained for the limits of hydrogen in air under pressures greater than atmospheric (*14, 17, 324*). The differences are not as great as they may appear to be at first sight, except for lower-limit mixtures at pressures of 1 to 5 atmospheres, and may well be ascribed to different interpretations of experimental results rather than to the experiments themselves; the criterion was 100-percent combustion for the series indicated in the figure by small circles but only about 80 percent for the series represented

by the unbroken line. In general, it appears that the limits are at first narrowed by increase of pressure above atmospheric but at higher pressures are steadily widened.

A series of experiments (*95*) besides those recorded in figure 5 showed no change in the lower limit over a range from 0.5 to 4 atmospheres. Other experiments made in a narrow tube, with downward propagation of flame and ignition by the fusion of a copper wire, gave low results for the higher limit (*51*).

Reduced pressure affected the lower limit as follows: In a closed glass tube 6.0 cm. in diameter and 120 cm. in length, with downward propagation of flame, at 1 atmosphere the lower limit was 9.35 percent and at ½ atmosphere, 10.6 percent (*325*). Experiments in a burette indicated the existence of a small lowering of the lower limit between about 500 and 200 mm. pressure, followed by a rapid rise between 200 and 100 mm. (*84*). Other experiments in narrow tubes (8, 16, and 25 mm. diameter), with upward propagation of flame, showed no great change in the limits until the pressure was below about 300 mm., when the range narrowed until below 50 mm. no mixture propagated flame (*96*).
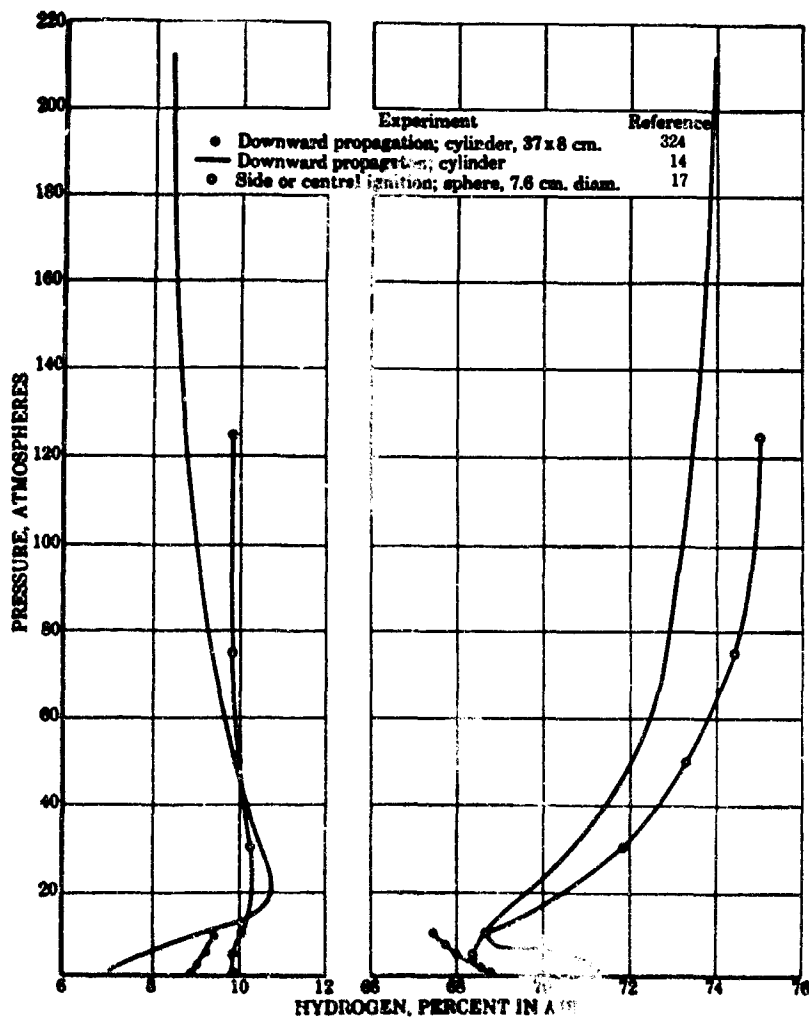
FIGURE 5.—Effect of Pressures Above Normal on Limits of Hydrogen in Air.

Influence of Temperature.—Three sets of observations have been made on the influence of temperature on the limits of hydrogen in air (*12, 297, 358*). Table 2 and figure 6 give those that are probably most reliable (*358*). They were determined in a closed tube 2.5 cm. in diameter and 150 cm. in length, with downward propagation of flame.

At 540° C. a 90.45-percent mixture was inflamed (*287*).

The flame temperature (table 2) necessary to insure propagation of flame downward is much above the ignition temperature of hydrogen in air, 585° C. Moreover, increase in initial temperature of the mixture does not cause the calculated flame temperature to fall toward the ignition temperature but has the opposite effect for lower-limit mixtures; this observation awaits explanation.

TABLE 2.—*Influence of temperature on the limits of flammability of hydrogen in air, downward propagation of flame*

Temperature, ° C.	Limits of flammability, percent hydrogen		Calculated flame temperatures, ° C	
	Lower	Higher	Lower limit	Higher limit
17±3	9.4	71.5	815	980
50	9.2		820	
100	8.8	73.5	825	970
150	8.3		830	
200	7.9	76.0	845	975
250	7.5		860	
300	7.1	79.0	875	970
350	6.7		890	
400	6.3	81.5	900	980

Influence of Impurities.—The lower limit of hydrogen in air, with downward propagation of
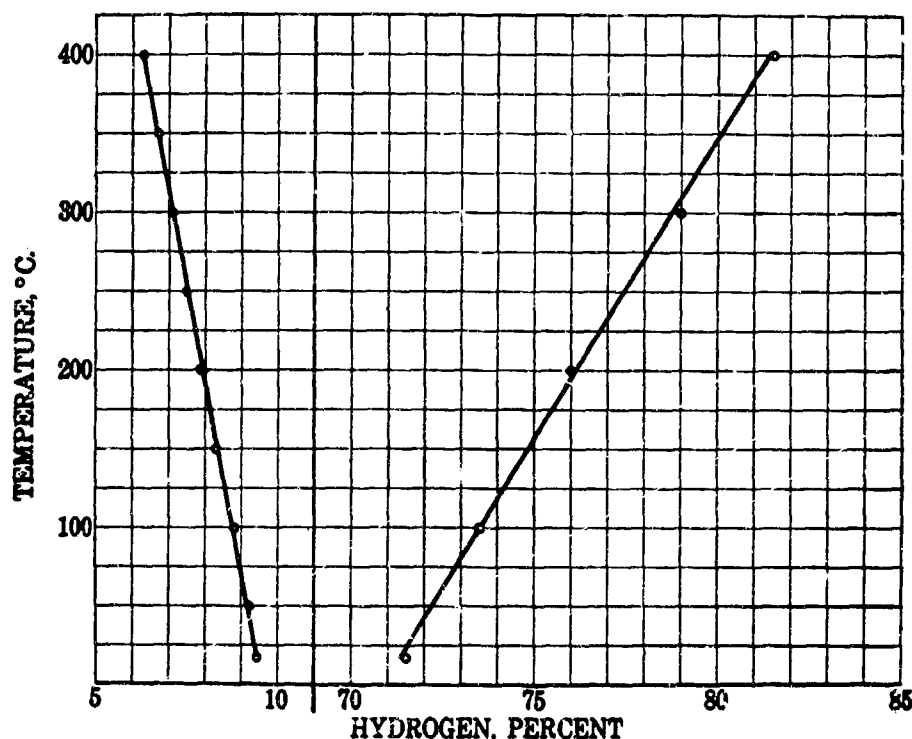
FIGURE 6.—Influence of Temperature on Limits of Flammability of Hydrogen in Air (Downward Propagation of Flame).

flame, was raised a fraction of 1 percent by the addition of iron carbonyl (0.028 and 0.056 cc. liquid vaporized per liter). The higher limit was reduced from 68 to 52 percent by the addition of iron carbonyl (0.024 cc. liquid vaporized per liter) (325).

HYDROGEN IN OXYGEN

The limits of visible flame of hydrogen in oxygen with upward propagation of flame in a tube 2 inches in diameter, open at the firing end, are 4.65 and 93.90 percent (150). In closed tubes the extremes recorded are 3.9 and 95.8 percent (56, 57, 78, 97, 274, 333). The lower-limit figures refer to the same type of flame as that of weak mixtures of hydrogen in air, and the lower limit in open vessels may prove to be as low as in closed vessels when special means are taken to detect an invisible flame.

For downward propagation of flame in small vessels the lower limit is about 9 or 10 percent hydrogen and the higher limit about 92, 93, or 94 percent (27, 57, 88, 95, 228, 274, 292, 323, 346).

For complete combustion of the gas in a 35-cc. spherical globe with side ignition the limits were 9.6 and 90.9 [b] percent hydrogen

[b] Probably too low. See footnote 4, table 1, p. 17.

(297); for inflammation in a closed bomb of 810-cc. capacity, 5 and 94.3 percent (349).

Influence of Pressure.—Experiments in a steel cylinder 3 inches in diameter and 5 inches in length, axis vertical, indicated that the lower limit of hydrogen in oxygen was not altered materially by increase of pressure to 122 atmospheres but lay between 8 and 9 percent throughout this range of pressure. Ignition was by spark or hot wire, and the direction of propagation of flame was presumably downward (254).

When the pressure is reduced below atmospheric, the higher limit falls slightly but does not reach 90 percent hydrogen (central ignition in a globe) until the pressure is about 100 mm., at which it is difficult to insure an adequate source of ignition; a powerful source of ignition might insure propagation of flame indefinitely in a hydrogen-oxygen mixture of 90 percent or a little more hydrogen at pressures below 100 mm. The lower limit does not rise above 11 percent hydrogen until the pressure is below 9 mm. (65).

Experiments in a burette indicated the existence of a small lowering of the lower limit between about 400 and 120 mm. pressure, followed by a rapid rise between 120 and 80 mm. (84).

Influence of Temperature.—In a 35-cc. closed bulb the limits were 9.6 and 90.9 percent at 15° C. and 9.1 and 94 percent at 300° C. (*297*).

HYDROGEN IN OTHER ATMOSPHERES

All Atmospheres of Oxygen and Nitrogen.—The limits of hydrogen in various mixtures of oxygen and nitrogen have been determined at 600 mm. and lower pressures, with downward propagation of flame in a tube 3 cm. in diameter (*88*). (*See also* Ammonia Contact Gas.)

Atmospheres of Composition Between Air and Pure Oxygen.—With downward propagation of flame in a Bunte burette, the lower limit fell gradually from 9.45 percent hydrogen in air to 9.15 percent in nearly pure oxygen. The higher limit rose from 65 percent hydrogen in air to 81 percent in a 40-percent oxygen mixture, 86 percent in a 56-percent oxygen mixture, and 91.6 percent in nearly pure oxygen (*323*).

In a mixture of equal volumes of oxygen and nitrogen, 91.35 percent hydrogen inflamed at 537° C. (*216*).

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of hydrogen in all mixtures of air and nitrogen, or air from which part of the oxygen has been removed,

are shown in figure 7. The determinations were made in a tube 6 feet in length and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation (*133*). From the ordinates of the "nose" of this curve it may be calculated that no mixture of hydrogen, nitrogen, and air at atmospheric pressure and temperature can propagate flame if it contains less than 4.9 percent oxygen (*167*).

For some purposes the results are more useful when expressed (*62*) as in figure 8.

This figure shows, for example, that a mixture containing 20 percent H_2, 6 percent O_2, and 74 percent N_2 is flammable; but if 2 percent of the oxygen were replaced by nitrogen the mixture would not be flammable but would become so by admixture with a suitable amount of air. In figure 8, "impossible mixtures" cannot be produced by mixing air, nitrogen, and hydrogen. For more detailed explanations, compare the corresponding section on methane limits in mixtures of air and nitrogen (pp. 44 to 48).

The limits with downward propagation of flame in the same series of mixtures have been determined in a closed tube 5 cm. in diameter and 65 cm. in length. The lower limits are 5 to 6 percent greater and the higher —1 to +10
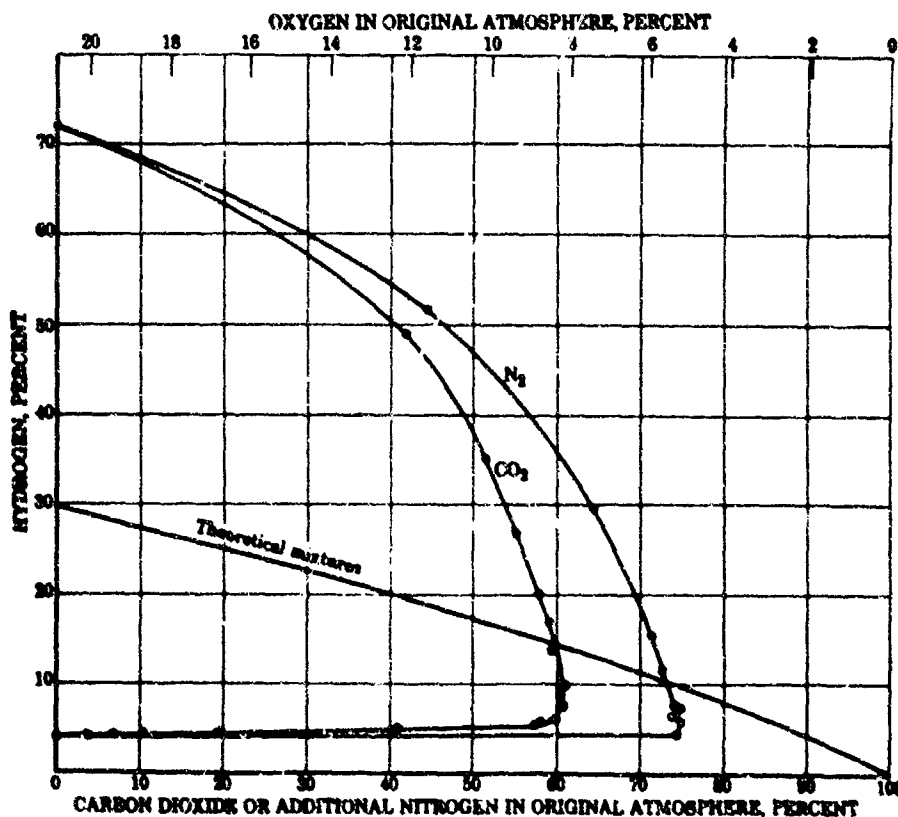
FIGURE 7.—Limits of Flammability of Hydrogen in Air and Carbon Dioxide or Nitrogen.
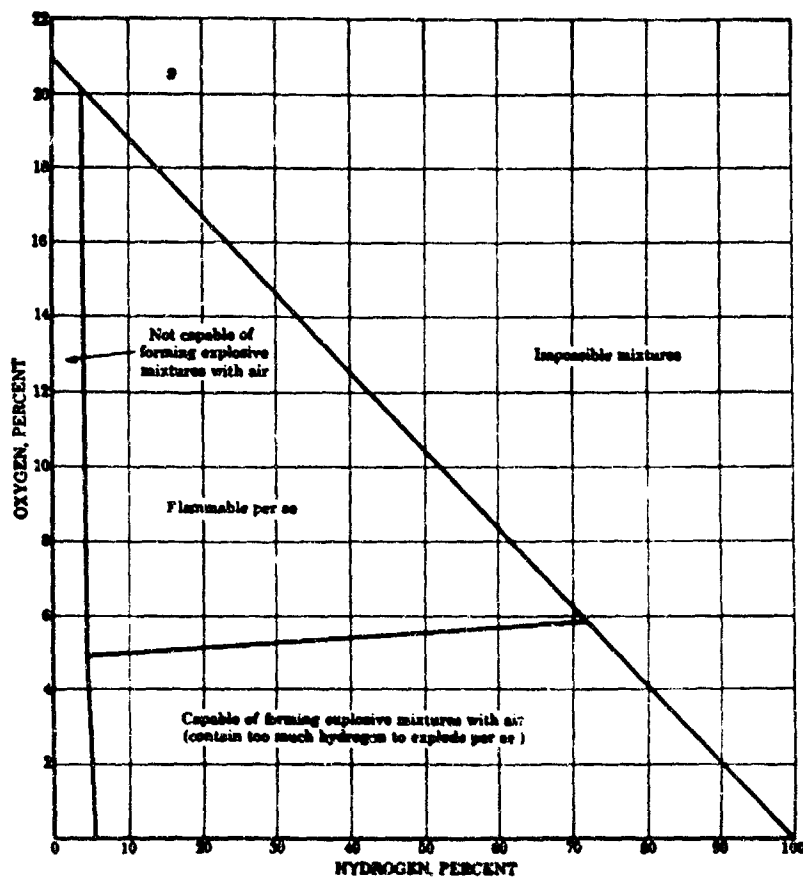
FIGURE 8.—Relation Between Composition and Flammability of Mixtures of Hydrogen, Oxygen, and Nitrogen.

percent greater than those of figure 7. The "nose" of the curve is at the same percentage of additional nitrogen. The addition of 0.5 percent of tin tetramethyl reduces the higher limit and retracts the "nose" of the curve considerably (318). The limits for downward propagation in a closed tube 2.2 cm. in diameter have also been determined (341).

Atmospheres of Air and Water Vapor.—The limits of hydrogen-air mixtures standing over water in a 350-cc. spherical vessel, and ignited near the water surface, have been determined at various temperatures. As the temperature rises, and consequently the water-vapor content also, the lower limit rises slowly, and the higher limit falls rapidly, as with other diluents. When 60 percent of water vapor is present (86° C.) the limits coincide at about 10 percent hydrogen (368).

Earlier experiments, made in a Bunte burette, show similar effects but the range of flammability is smaller (95).

Atmospheres of Air and Carbon Dioxide.—The limits of flammability of hydrogen in all

mixtures of air and carbon dioxide are shown in figure 7. The determinations were made in a tube 6 feet in length and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation (133, 167).

The limits with downward propagation of flame in the same series of mixtures have been determined in a closed tube 5 cm. in diameter and 65 cm. in length. The lower limits are 5 to 6 percent greater and the higher limits 1 to 4 percent less than those in figure 7. The "nose" of the curve is at 56 percent carbon dioxide in the atmosphere. The addition of 0.5 percent tin tetramethyl reduces the higher limit and retracts the "nose" of the curve considerably (318). The limits with downward propagation in closed tubes 2.2 and 1.6 mm. in diameter have also been determined (217, 341).

Some earlier observations (95) show, as might be expected, a more rapid narrowing of the limits in a Bunte burette. Others (1) may be mentioned, but they can hardly be accepted without confirmation because they indicate several improbable conclusions—for example,

that the lower limit of hydrogen is reduced from 6.5 percent in air to 3 percent in an atmosphere composed of air and 3 or 4 percent of carbon dioxide.

Atmospheres of Air and Helium.—When thin rubber balloons 2.5 inches in diameter were filled with various mixtures of hydrogen and helium and a lighted match or a white-hot platinum spiral was used to burn a hole in the fabric, the hydrogen could be raised to 26 percent before the mixture became flammable, but if the hydrogen exceeded 28 percent the mixture would burn. Hence, it was concluded that to dilute the helium used for airships with more than about 26 percent of hydrogen (296) would not insure safety against inflammation of the gas.

Experiments by the present writers show that homogeneous mixtures of helium, hydrogen, and air would propagate flame when the proportion of hydrogen to helium is much less than that indicated above. When as little as 8.7 percent hydrogen is present in admixture with helium, it is possible to make, with this mixture, a blend with air that will propagate a weak flame up through the central part of a tube 2 inches in diameter and 6 feet in length. The complete set of observations is shown in table 3.

TABLE 3.—*Limits of flammability of mixtures of hydrogen and helium in air, upward propagation of flame in tube 2 inches in diameter and 6 feet in length, open at its lower end*

Original gas mixture, percent		Limits of flammability, percent	
Hydrogen	Helium	Lower	Higher
100.0	0	4.2	71.5
96.1	41.9	7.1	76.2
77.9	72.1	16.6	79.2
19.3	80.7	21.9	81.2
10.7	89.3	31.3	80.3
8.7	91.3		69.5

The mixture that contained 19.3 percent hydrogen and the rest helium had very wide limits of flammability. Flame traveled rapidly and with some violence through mixtures with air that lay well within these limits, although the balloon experiments had seemed to show that these mixtures were nonflammable. No mixture would be safe for use in an airship unless it contained less than 8.7 percent hydrogen in admixture with helium (72).

With downward propagation of flame in a closed tube 2.2 cm. in diameter the weakest mixture of hydrogen and helium that can form a flammable mixture with air contains about 12 percent hydrogen (341).

The maximum amount of hydrogen that could be added to helium without enabling the mixture to burn when issuing into air from a jet 15 mm. in diameter, ignition by a gas flame, was 14 percent (223). •

Atmospheres of Air and Argon.—The limits of hydrogen in mixtures of air and argon, with downward propagation of flame in a closed tube 2.2 cm. in diameter, have been determined (341).

Atmospheres of Air and Certain Halogenated Hydrocarbons.—A series of results showing the lower and higher limits of hydrogen in air containing increasing amounts of trichloroethylene at 14°, 25°, and 35° C. have been reported. They were observed in small burettes 15 mm. in diameter, so are of limited value (200). Similar experiments with the vapors of other chloro-derivatives at laboratory temperatures were reported in an earlier communication (195).

The addition of increasing amounts of methyl bromide to the air causes the limits of hydrogen to approach, and in a 2-inch-diameter tube, to meet when 13.7 percent of the mixture is methyl bromide. The lower limit of hydrogen is, however, appreciably reduced (down to 2.4 percent with 12 percent of methyl bromide), showing that the bromide takes some part in the combustion (38). The results are of doubtful applicability to wide spaces, for with a sufficiently powerful source of ignition some mixtures of methyl bromide alone and air can be inflamed (p. 101).

The addition of increasing amounts of dichlorodifluoromethane ("freon") to the air causes the limits of hydrogen to approach and, in a 2-inch-diameter tube, to meet when 35 percent of the mixture is freon (38).

Atmosphere in Which Nitrogen of Air Is Replaced by Carbon Dioxide.—The limits of hydrogen in this atmosphere, with upward propagation of flame in a 5.3-cm.-diameter tube open at the lower end, are 5.31 and 69.8 percent, as compared with 4.19 and 74.6 percent, respectively, in air. For downward propagation in the same tube, the upper end being open, the lower limit is 13.1 percent as compared with 9.0 percent in air (94).

In a closed 2.5-cm.-diameter tube, with upward propagation of flame, the limits are 4.7 and 70.3 percent; the range is narrower in narrower tubes (98).

In a closed 35-cc. globe with side ignition, the limits were 11.9 and 68.2 percent hydrogen compared with 9.4 and 64.8 percent, respectively, in air in the same apparatus (297). The higher-limit result is unexpectedly greater in the artificial atmosphere than in air; a similar result, however, had been obtained earlier (346). Reasons have already been given (footnote 4, table 1, p. 17) for thinking that the figure 64.8, for the higher limit in air, is too low.

Influence of Temperature.—Some irregular results have been obtained for the influence of temperature on the limits of hydrogen in an atmosphere of 21 percent oxygen and 79 percent carbon dioxide. They need confirmation (*297*). An isolated observation is that a mixture containing 82.9 percent hydrogen inflamed at 552° C. (*216*).

Atmospheres in Which Nitrogen of Air Is Replaced by Argon, Neon, or Helium.—The limits of hydrogen in atmospheres in which the nitrogen of the air is replaced by (*a*) argon or (*b*) helium, with upward propagation of flame in a 5.3-cm.-diameter tube open at the lower end, are (*a*) 3.17 and 76.4 percent and (*b*) 7.72 and 75.7 percent. For downward propagation in the same tube, the upper end being open, the lower limits are (*a*) 7.0 and (*b*) 8.7 percent (*94*).

In a closed 2.5-cm.-diameter tube, with upward propagation of flame, the limits are (*a*) 2.71 and 75.3 percent and (*b*) 5.9 and 71.8 percent; both ranges are narrower in narrower tubes (*98*).

In a mixture of 20.9 percent oxygen and 79.1 percent argon, 89.10 percent hydrogen inflamed at 545° C. (*216*). (*See also* Deuterium in Other Atmospheres.)

Atmosphere of Chlorine.—In a eudiometer tube about 1 cm. in diameter, with gases standing over sulfuric acid, the limits of hydrogen in chlorine, apparently for downward propagation of flame, were 8.1 and 85.7 percent. Radiation from burning magnesium ignited mixtures containing between 9.8 and 52.5 percent hydrogen (*237*).

The limits with downward propagation of flame in a tube 1.5 cm. in diameter and 30 cm. in length are 10.4 and 83.9 percent hydrogen. Reasons are given for preferring these figures to those given above (*228*).

In an iron bomb of 810-cc. capacity, the limits of hydrogen in chlorine are 6 and 84.5 percent (*349*).

With a spark discharge or a heated platinum spiral in a half-liter cylinder 4 cm. in diameter, the apparent limits of hydrogen in chlorine vary with circumstances; the widest range was 5.5 to 89 percent. Results are also given for mixtures to which hydrogen chloride, nitrogen, oxygen, and carbon dioxide were added (*214*).

Atmospheres of Chlorine and Nitrogen; Chlorine and Oxygen; Chlorine and Nitric Oxide; Chlorine, Nitric Oxide, and Nitrogen.—The limits of ternary mixtures of hydrogen with each of these mixtures are given in triangular diagrams for downward propagation of flame (*228*).

Atmospheres of Oxygen and (1) Hydrogen Chloride, (2) Carbonyl Chloride, and (3) Difluorodichloromethane.—The limits of ternary mixtures of hydrogen, oxygen, and each of these substances are given in triangular diagrams for downward propagation of flame in a 1.6-cm.-diameter tube (*335*).

Atmosphere of Nitrous Oxide.—The limits of hydrogen in nitrous oxide, with downward propagation of flame in a 16-mm. burette, are 5.2 and about 76 percent (*285*); in a 15-mm. tube, 5.6 and 79.7 percent (*339*). The effect of a diluent in narrowing the limits increases in the following order: Argon, nitrogen, carbon dioxide, helium (*285*).

Atmosphere of Nitric Oxide.—The limits of hydrogen in nitric oxide (wrongly called nitrous oxide by the author, a Netherlands chemist writing in English) with downward propagation of flame in a tube 15 mm. in diameter are 13.5 and 49.4 percent (*228*).

Atmospheres of Nitrous and Nitric Oxides.—The region of flammability of mixtures of hydrogen with mixtures of nitrous and nitric oxides is plotted in a triangular diagram (*239*), but the spark used was too weak to ignite any mixture of hydrogen and nitric oxide alone (*228*).

Atmospheres in Which Oxygen of Air Is Replaced by Nitrous Oxide.—The limits of hydrogen in a mixture of 21 percent nitrous oxide and 79 percent nitrogen, with upward propagation of flame in a 5.3-cm.-diameter tube open at the lower end, are 4.19 and 29.0 percent. When the mixture contains 42 percent nitrous oxide and the amount of combined oxygen therefore equals the amount of free oxygen in air, the limits are 4.38 and 65.8 percent in the same experimental conditions, in comparison with 4.19 and 74.6 percent in air (*93*).

Influence of Small Amounts of "Promoters."—The addition of about 0.5 percent of various possible "promoters" (diethyl peroxide, ethyl nitrate, nitrogen peroxide, methyl iodide, ozone) had little effect on the lower limit of hydrogen in air and little more effect on the higher limit than that due to the thermal effects of their reactions (*93*).

Dilution of Electrolytic Gas ($2H_2 \cdot O_2$) With Gases, Inert or Otherwise.—In the early part of the last century the question of the amount of diluent that, mixed with electrolytic gas, would bring a mixture to its limit of flammability aroused much interest, which has been revived from time to time. Some of the diluents were inert; others were not. Table 4 gives the results.

The conditions of some of these experiments are very incompletely stated but can be surmised from the figures for the diluents hydrogen and oxygen, as limit mixtures made by diluting electrolytic gas with hydrogen and oxygen are the same as higher- and lower-limit mixtures, respectively, of hydrogen in oxygen. Thus,

Davy's, Turner's, and Bunsen's experiments probably were made with upward propagation of flame. Davy and Turner probably used fairly wide vessels and Bunsen a rather weak spark as the source of ignition. Regnault and Reiset, Von Meyer, Tanatar, Misteli, Eitner, and Jorissen observed downward propagation of flame.

Uncertainty as to some of the methods used and the small scale of the experiments make it impossible to draw exact conclusions from the results in table 4. In general, however, it is evident that the inert gases of higher heat capacity are more effective than those of lower heat capacity in rendering electrolytic gas nonexplosive. Helium is more effective than argon, presumably because of its greater thermal conductivity. Moreover, when the diluent is itself flammable and therefore competes with the hydrogen for the oxygen of the elecrolytic gas, it is even more extinctive of flame than the inert gases, provided that it contains several atoms capable of uniting with oxygen.

TABLE 4.— *Percentage of electrolytic gas which, with diluent named, is at limit of flammability* [1]

Diluent	Percentage and authority			Payman and Titman (274, 275) [2]	
	Davy (78)	Turner (333)		Up-ward	Down-ward
Hydrogen	11–14	10–12.5	21–23 (Bunsen, 27)	17.4	17.4
Oxygen	10–12.5	6.7–7.7	8.6–9.7 (Bunsen, 27), 13.9 (Eitner, 95)	5.9	13.6
Air		7.7–9.1			
Nitrogen			14.3 (Henry, 122), 19.2 (Eitner, 95)	15.5	16.8
Carbon dioxide		25–33	25–27 (Regnault and Reiset, 292), 25.7 26.2 (Bunsen, 27), 30.0 (Eitner, 95).	23.0	25.9
Helium				13.9	13.9
Argon				10.6	12.5
Hydrochloric acid	30–40	20–25			
Silicon fluoride	55–57				
Sulfur dioxide		33–50			
Nitrous oxide	8–9	10–12.5			
Carbon monoxide		20–25		17.1	17.1
Hydrogen sulfide	33–40	67–80	50 approximate (Budde, 25)		
Ammonia		50–67	50 (Partington and Prince, 268) [3]		
Methane	50–57		76–78 (Tanatar, 320), 76 (Misteli, 217)		
Ethane			85.5–85.7 (E. von Meyer, 248)		
Ethylene	67–75	50–67	78.6–80.8 (E. von Meyer, 248), 75 (Misteli, 217), 80 (Jorissen, 202).		
Propylene			88–89 (Tanatar, 320), 85–86 (Misteli, 217)		
Trimethylene			88–89 (Tanatar, 320)		
Acetylene			50 (Tanatar, 320)		
Cyanogen			40 (Henry, 122)		
Coal gas		67–80			

[1] Of 2 figures, the lower represents a nonflammable mixture and the higher a flammable mixture.
[2] In a closed tube 2.2 cm. in diameter and 45 cm. in length.
[3] At 85° C. and 340 mm. pressure.

PARA-HYDROGEN

The lower limit of para-hydrogen in air with upward propagation of flame in a tube 7 cm. in diameter and 120 cm. in length is between 4.3 and 4.5 percent. Under the same conditions, the lower limit of ordinary hydrogen is between 4.3 and 4.4 percent. The higher limit of a mixture of equal parts of ortho- and para-hydrogen was not less than that of ordinary hydrogen (114).

DEUTERIUM

DEUTERIUM IN AIR AND IN OXYGEN

The limits of deuterium, which have been observed only in closed vessels, are given in table 5, with those for hydrogen obtained by the same observers in parallel experiments.

The ratio of figures (56) with upward propagation (deuterium and hydrogen in air) is almost equal to the inverse ratio of the diffusion coefficients of the two gases, a fact that agrees

with the explanation given (p. 11) for the peculiar nature of the lower-limit flame of hydrogen.

DEUTERIUM IN OTHER ATMOSPHERES

The lower limits of deuterium and hydrogen in mixtures of 20 percent of oxygen and 80 percent of various chemically inert gases, at 400 mm. pressure, have been determined in a closed tube 4.5 cm. in diameter and 80 cm. in length. They are as follows:

Atmosphere	Upward propagation of flame		Downward propagation of flame	
	Deuterium	Hydrogen	Deuterium	Hydrogen
Nitrogen, 80 percent	5.65	3.9	0	9.6
Helium, 80 percent	7.4	5.8	8.4	8.1
Neon, 80 percent	4.3	5.55	7.7	7.1
Argon, 80 percent	3.75	2.7	7.2	7.1

The three last-named gases have equal specific heats but different densities and thermal conductivities. In the helium mixtures the convection is least and the dissipation of the energy of the flame front by diffusion the greatest; correspondingly, the limit is the highest and the difference in the limits with upward and downward propagation of flame the least (57).

Dilution of $2D_2+O_2$.—The limits of $2D_2+O_2$ in various diluents, with downward propagation of flame in a closed tube 2.2 cm. in diameter, are (274):

Diluent:

Percentage of $2D_2+O_2$ which, with diluent named, is at limit of flammability

Deuterium _____ 15.9
Nitrogen _____ 16.8
Oxygen _____ 15.3

TABLE 5.—*Limits of flammability of deuterium and hydrogen in air*

Upward Propagation of Flame

Pressure, mm.	Dimensions of tube, cm.		Deuterium limits, percent				Hydrogen, limits, percent				Reference No.
	Diameter	Length	In air		In oxygen		In air		In oxygen		
			Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher	
400	4.5	80	5.65				4.4				56
760	2.2	45	4.9	75.0	4.9	94.7	3.9	73.0	3.5	94.2	274
400	4.5	80	5.65		5.7		3.9		3.9		57

Downward Propagation of Flame

400	4.5	80	11.0				9.6				56
760	2.2	45	10.2	75.0	10.2	94.7	9.1	73.0	9.1	94.2	274
400	4.5	80	11.0		11.1		9.6		9.5		57

AMMONIA

AMMONIA IN AIR

Tests in which atmospheric pressure was maintained during the propagation of flame do not appear to have been made with ammonia-air mixtures; but this condition was approached in one research (280), included in table 6, in which a rubber stopper at the top of the test vessel usually jumped from its seating.

Influence of Pressure.—In an apparatus in which the only mixture of ammonia and air that could be inflamed at atmospheric pressure contained 21.9 percent ammonia, the limits at 16 atmospheres were 17.1 and 28.8 percent ammonia, and at 36 atmospheres the lower

limit was about 17 percent. Ignition was attempted by the electric fusion of a silver wire (10). In the 50-liter bomb (107) the lower limit was unchanged between 1 and 20 atmospheres pressure.

Influence of Temperature.—The range of flammability of ammonia-air mixtures is widened as the temperature is raised to 450° C., as shown by figure 9. A closed tube 5 cm. in diameter was used. The calculated flame temperature for the lower limits, horizontal propagation, is almost constant; therefore the preliminary heating of the mixture seems merely to save the necessity, so to speak, for liberation of the same amount of heat by combustion (354).

TABLE 6.—*Limits of ammonia in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Tube	Limits, percent		Content of aqueous vapor, percent	Reference No.
Diameter	Length		Lower	Higher		
7. 5	150	Closed	17. 1	26. 4	0. 4–2. 5	*354*
6. 0		(See text)	15. 0	28. 0	Dried	*280*
5. 0	150	Closed	16. 1	26. 6	0. 4–2. 5	*354*
5. 0	150	do	16. 1	26. 6		*130*

Horizontal Propagation of Flame

7. 5	150	Closed	17. 4	26. 3	0. 4–2. 5	*354*
5. 0	150	do	18. 2	25. 5	0. 4–2. 5	*354*

Downward Propagation of Flame

7. 5	150	Closed	No propagation		0. 4–2. 5	*354*
5. 0	150	do	do			*130*
1. 6		do	do			*301*

Propagation Throughout a Spherical Vessel or a Bomb

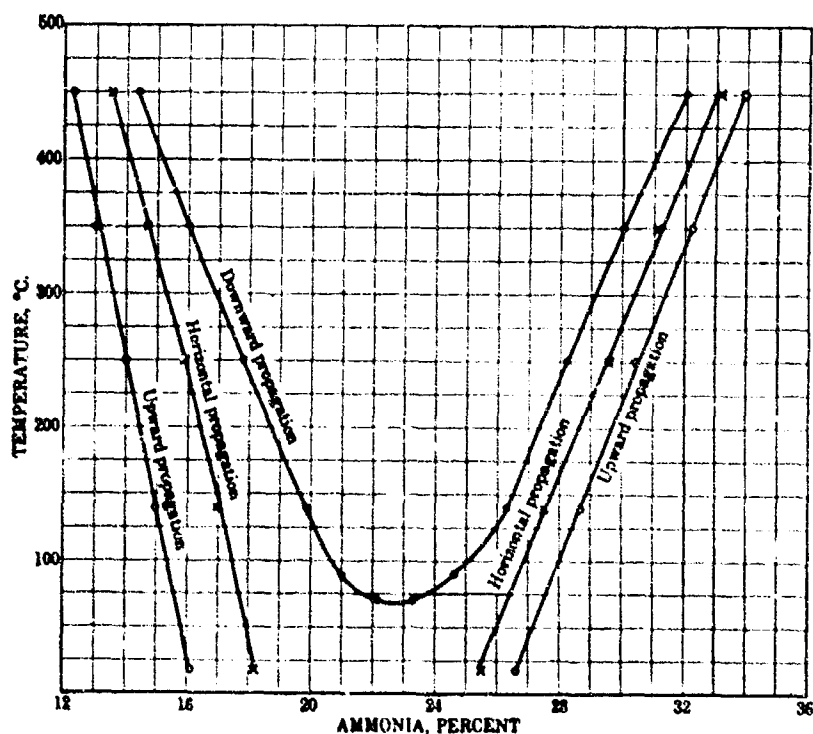|						
Sphere, 0.5 liter		Closed	16. 5	26. 8	1	*301*
Cylinder, 1.2 liters		do	16. 0	25. 0		*256*
Bomb, 50 liters		do	16. 0			*197*

FIGURE 9.—Limits of Flammability of Ammonia-Air Mixtures; Influence of Temperature and of Direction of Propagation of Flame.

If the mixture of ammonia and air stands over an aqueous solution of ammonia (strength not stated) the limits are rapidly narrowed by rise of temperature until at about 44° C. they meet. Above this temperature the amount of water vapor is sufficient to render all mixtures of ammonia and air nonflammable (300).

AMMONIA IN OXYGEN

The earliest recorded limits known to the present writers are those for ammonia in oxygen. In 1809 W. Henry wrote "With a greater proportion of pure oxygen gas to ammonia than that of 3 : 1, or of ammonia to oxygen than that of 3 : 1.4, the mixtures cease to be combustible" (121). These proportions correspond with 25 and 68 percent ammonia, respectively.

Table 7 gives modern determinations of the limits of ammonia in oxygen, in closed tubes.

In a glass bulb 100 cc. in capacity the limits at 85° C. and 380 mm. pressures are 21 and 74.5 percent (268).

In a 50-liter bomb the limit for complete inflammation when ignition was central depended on the nature of the source of ignition. The lower limit, ignition by electric spark or guncotton, was 15.9 percent; by a mixture of sulfur and potassium chlorate, 13.5 percent (107).

From observations with a split Bunsen flame the lower limit of ammonia in oxygen was estimated as somewhat less than 15 percent and the higher limit as somewhat greater than 80 percent (293).

Influence of Pressure.—In a 50-liter bomb the lower limit for complete combustion was 13.5 percent at 1, 12.0 at 5, 10.8 at 10, and 10.0 at 20 atmospheres (107).

TABLE 7.—Limits of ammonia in oxygen (closed tube)

Dimensions of tube, cm.		Direction of propagation						Reference No.
		Upward		Horizontal		Downward		
Diameter	Length	Lower	Higher	Lower	Higher	Lower	Higher	
7. 5	150	14. 8	..	15. 6	.	17. 3	....	354
5. 0	150	15. 3	79	16. 7	79	18. 1	79	354
1. 7	..	...	..	...	..	21. 0	64. 6	345
1. 5	..	...	..	....	..	18. 9	69. 3	203

Influence of Temperature.— In a closed tube 5 cm. in diameter the following figures were obtained for the lower limit (354):

Lower limit of ammonia in oxygen (closed tube)

Temperature	° C	18	250	450
Horizontal propagation	percent	16.7	14.6	12.6
Downward propagation	do	18.1	15.8	13.5

AMMONIA IN OTHER ATMOSPHERES

Atmospheres of Oxygen and Nitrogen, of Oxygen and Carbon Dioxide, and of Oxygen and Argon.—The limits of ammonia in these mixtures have been determined with downward propagation of flame in 1.5- and/or 1.7-cm.-diameter tubes (203, 345).

Atmosphere of Nitrous Oxide.—A very old determination gave the limits of ammonia in nitrous oxide, conditions not stated, as about 17 and 67 percent (124). Recently, these limits have been deduced by small extrapolations of the limits found in series of mixtures of nitrous oxide and air. They were determined for upward, horizontal, and downward propa-

gation of flame in closed 2- and 3-inch-diameter tubes, as follows:

Limits of ammonia in nitrous oxide (closed tube)

Tube diameter, cm.	Upward		Horizontal		Downward	
	Lower	Higher	Lower	Higher	Lower	Higher
7.5	¹2.2	71.9	4.4	71.7	(¹)	71.7
5.0	2.6	71.9	5.1	71.6	6.8	71.0

¹ Tube burst with limit mixture.

The lower limits were difficult to determine because violent explosions sometimes occurred, shattering the tubes, with mixtures below the limit for normal flame propagation. This is ascribed to the exothermic decomposition of nitrous oxide sensitized by small amounts of ammonia (130).

Increase of temperature widens the range appreciably at the lower limit, slightly at the higher limit (130).

Atmospheres of Air and Nitrous Oxide.—The limits of ammonia in various mixtures of air

and nitrous oxide, with upward, downward, and horizontal propagation of flames, have been determined in a 2-inch-diameter closed tube. They accord fairly closely with Le Chatelier's rule, that is, mixtures of limit mixtures of the same sort (lower or higher) are themselves limit mixtures (130).

Atmosphere of Nitric Oxide.—The limits of ammonia in nitric oxide, with downward propagation of flame in a tube 1.8 cm. in diameter, are approximately 20 and 65 percent (339).

HYDRAZINE

HYDRAZINE IN AIR

The limits of hydrazine in air, with upward propagation of flame in a 1-inch-diameter tube open at the upper end, are 4.67 and 100 percent at about 100° C. Hydrazine decomposes exothermically, and its vapor can propagate flame down to 12 mm. pressure (at 29° C.) without the assistance of air or other supporter of combustion (304).

The limits of 85 percent hydrazine hydrate in air, determined similarly and calculated on the assumption of complete dissociation of the hydrate at the temperature of the tests (about 100° C.), are equivalent to 5.95 and 27.37 percent N_2H_4 (304).

HYDRAZINE IN OTHER ATMOSPHERES

Hydrazine vapor mixed with various diluents is capable of propagating flame within the following concentrations, at temperatures ranging from 104° to 135° C. and roughly atmospheric pressure (304):

Diluent	Hydrazine limits, percent	
	Lower	Higher
Nitrogen	38.0	100
Helium	37.0	100
Water	30.9	100
Heptane	86.8	100

With a spark which gave a pressure limit of 35 mm. for pure hydrazine, the following results were obtained. At 135 mm. (and 100° C.) the lower limit in nitrogen is 48.6 percent; at 147 mm. in ammonia it is 61.2 percent; at 332 mm. in $5N_2 + NO$ it is 27.1 percent (5).

HYDROGEN SULFIDE

HYDROGEN SULFIDE IN AIR

In a horizontal tube 6 cm. in diameter and open at both ends the limits of hydrogen sulfide in air were 5.9 and 27.2 percent (182).

In closed tubes 1.5 meters in length and of different diameters the limits for mixtures containing 1 percent water vapor were as follows (356):

Limits of hydrogen sulfide in air (1 percent water vapor) in closed tubes, percent

Diameter of tube, cm.	Direction of propagation of flame					
	Upward		Horizontal		Downward	
	Lower	Higher	Lower	Higher	Lower	Higher
5.0	4.40	44.5	5.40	26.6	6.05	19.8
7.5	4.30	45.5	5.30	35.0	5.85	21.3

The limits in a closed horizontal tube, 4.5 cm. wide and 75 cm. long with spark ignition at the center, are given as 3.1 and 45.1 percent (283). The great difference between these figures and the corresponding figures in the tabulation above was not discussed.

HYDROGEN SULFIDE IN OTHER ATMOSPHERES

Atmospheres of Nitrogen and Oxygen.—The lower limit of hydrogen sulfide, with downward propagation of flame in a closed glass tube 150 cm. in length and 5 cm. in diameter, fell steadily from 6.60 percent in 15.6 percent oxygen to 4.93 in 66.6 percent oxygen (360).

Atmospheres of Air and Carbon Dioxide.—With increasing amounts of carbon dioxide added to air, the limits of hydrogen sulfide approach and ultimately meet. In a closed horizontal tube 4.5 cm. wide and 75 cm. long with spark ignition at the center, about 25 percent of carbon dioxide in the mixture is sufficient to prevent any mixture inflaming completely, and about 36 percent prevents partial inflammation (283).

Atmosphere of Nitric Oxide.—The limits of hydrogen sulfide in nitric oxide, with downward propagation of flame in a tube 18 mm. in diameter, are approximately 29 and 55 percent (339).

HYDROGEN CYANIDE (PRUSSIC ACID)

The limits of hydrogen cyanide in air are said to be 12.75 and 27 percent, but the experimental conditions were not stated (52). Later reports give 5.6 and 40.0 percent (255) and, in a 50-cc. pipette, 7 and 41 percent (279) as the limits. A figure of "around 8 percent" is quoted for the lower limit in unstated conditions (16).

Influence of Pressure.—In a 50-cc. pipette the range of flammability narrows with reduction of pressure, the limits meeting at about 50 mm. (279).

CYANOGEN

Table 8 gives observed limits of flammability of cyanogen in air (265). Other observations, under unstated conditions, gave the limits 7.6 and 38.0 percent (326), and, in small vessels, 9.8 and 24.6 percent (8) and 6.6 and 42.6 percent (9).

For the results tabulated, ignition was by electric spark between tungsten electrodes 4 to 5 mm. apart. No dry mixture was ignitible by this spark in the two wider tubes, but a brightly red-hot tungsten filament in the 2.5-cm.-diameter tube ignited mixtures within the range 19 to 26 percent cyanogen, after a delay of up to 30 seconds. The resulting ignition resembled a detonation and shattered the tube.

Within the range given in the table for each of the higher-limit figures, propagation was obtained if the tube had been evacuated to 0.01 mm. before introduction of the mixture, but not if it had been evacuated to 0.001 mm. for at least 15 minutes (265).

Influence of Pressure.—The effect of reduced pressure on the limits of ignitibility by a weak standard spark, rather than on the limits of flammability, has been examined (8).

TABLE 8.—*Limits of flammability of cyanogen in air*

Upward Propagation of Flame

| Dimensions of tube, cm. | | Tube | Limits, percent | | Content of aqueous vapor |
Diameter	Length		Lower	Higher	
3.5	60	Closed	6.15	30.8–32.0	Nearly saturated.
2.5	60	do	6.3	29.8–31.0	Do.
2.0	60	do	6.55	29.0–30.1	Do.
2.0	60	do	18.0	28.0–28.8	Dry.
1.5	60	do	7.1	28.35–29.3	Nearly saturated.
1.5	60	do	17.25	29.2–30.1	Dry.

Downward Propagation of Flame

| Dimensions of tube, cm. | | Tube | Limits, percent | | Content of aqueous vapor |
Diameter	Length		Lower	Higher	
3.5	60	Closed	6.4	30.1–30.6	Nearly saturated.
2.5	60	do	6.45	28.2–28.7	Do.
2.0	6	do	6.70	27.3–27.9	Do.
2.0	60	do	18.5	25.35–25.8	Dry.
1.5	60	do	7.25	26.2–26.7	Nearly saturated.
1.5	60	do	17.7	26.2–26.6	Dry.

CARBON DISULFIDE

CARBON DISULFIDE IN AIR

The limits of carbon disulfide in air with upward propagation of flame in a tube 6 cm. in diameter and 180 cm. in length, open at the firing end, are about 1.35 and 44.5 percent (185); in a tube 5 cm. in diameter, 1.25 percent is the lower limit (138).

Table 9 summarizes other determinations of the limits of carbon disulfide in air.

Two older determinations are replaced by the foregoing results (213, 240). A determination in a very small vessel gave the limits as 0.8 and 52.6 percent (9).

Abnormal Influence of Small Quantities of a Third Substance.—Introduction of 0.1 or 0.2 percent of certain substances into the air raises the lower limit (downward propagation of flame) of carbon disulfide from 1.9 to about 3.0

percent. Examples of these are pentane, ether, acetaldehyde, ethylene, alcohol, and acetylene. Other substances of similar action, but not so marked, are benzene, acetone, hydrogen sulfide, acetic acid, methane, and hydrogen. Carbon monoxide, cyanogen, and nitrogen have little, if any, such action. It has been suggested that, as the lower limit of carbon disulfide is much less, compared with that of most other substances, than its heat of combustion would indicate, its combustion is catalyzed by a product of incomplete combustion, perhaps carbon monosulfide, and the catalyst is readily poisoned by such substances as pentane (360).

Small amounts of diethyl selenide, tin tetramethyl, and lead tetramethyl have a similar effect; 0.2 percent of these substances raises the lower limit for downward propagation of flame in a 5-cm. tube from 1.90 to 3.70, 3.45, and 3.00 percent, respectively (250).

TABLE 8.—*Summary of other determinations of limits of carbon disulfide in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Far end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length			Lower	Higher		
7. 5	150	Closed_____	Closed_____	1. 06	_____	Dry_____	*353*
5. 0	150	_____do_____	_____do_____	1. 41	[1] 50. 0	_____do_____	*353*
2. 5	150	_____do_____	_____do_____	1. 71	_____	_____do_____	*353*

Horizontal Propagation of Flame

Diameter	Length	Firing end	Far end	Lower	Higher	Content	Reference
7. 5	150	Closed_____	Closed_____	1. 67	_____	Dry_____	*353*
5. 0	150	_____do_____	_____do_____	1. 83	[1] 49. 0	_____do_____	*353*
2. 5	150	_____do_____	_____do_____	2. 08	_____	_____do_____	*353*

Downward Propagation of Flame

Diameter	Length	Firing end	Far end	Lower	Higher	Content	Reference
7. 5	150	Closed_____	Closed_____	1. 91	35. 0	Dry_____	*353*
5. 0	150	_____do_____	_____do_____	2. 03	34. 0	_____do_____	*353*
5. 0	65	Open (?)_____	_____do_____	1. 90	37. 0	_____	*250*
2. 5	150	Closed_____	_____do_____	2. 08	31. 0	Dry_____	*353*
Bottle, 2 liters_____		Open_____	_____do_____	1. 94	_____	_____	*221*

[1] At 60° C.

Influence of Pressure.—The effect of reduced pressure on the limits of ignitibility by a weak standard spark of carbon disulfide in air, rather than on its limits of flammability, have been examined (*8*). Higher limits at 90 to 210 mm. pressure have been given for a 50-cc. pipette (*279*).

CARBON DISULFIDE IN OTHER ATMOSPHERES

Nitrogen and Oxygen.—The lower limit of carbon disulfide, with downward propagation of flame in a closed glass tube 5 cm. in diameter and 150 cm. in length, fell steadily from 2.63 percent in 11.8 percent oxygen to 2.00 in air and 1.24 in 93 percent oxygen (*360*).

Air and Carbon Dioxide.—One volume of carbon disulfide needs 22.2 volumes of carbon dioxide to make a mixture that is nonflammable in air (*185*). The higher limits at reduced pressures have been given for some mixtures in a 50-cc. pipette (*279*).

Air and Carbon Tetrachloride.—One volume of carbon disulfide needs 5.2 volumes of carbon tetrachloride to make a mixture that is non-flammable in air. This figure is much reduced by adding to the carbon disulfide 5 to 20 percent ethyl bromide, tin tetramethyl, or gasoline (boiling point, 45° to 50°) (*251*). Another observation is that 1 volume of carbon disulfide needs 7 to 9 volumes of carbon tetrachloride to make a mixture that is nonflammable in air

(downward propagation of flame) (*290*). Another result seems impossibly small (*282*).

Air and Other Substances.—All mixtures of air and carbon disulfide are rendered nonflammable (downward propagation of flame) by 55 percent of a mixture of 23.6 percent carbon dioxide and 76.4 percent nitrogen, by 20 percent ammonia, or by 45 percent sulfur dioxide (*290*).

Nitrous Oxide, Nitric Oxide, and Nitrogen Peroxide.—The limits of flammability of carbon disulfide in nitrous oxide in an electric light bulb (ignition by fusion of a wire) were about 1 and 52 percent at 350 mm. pressure. As the pressure is reduced, the limits approach each other, and below 14 mm., no mixture is flammable (*344*). The limits in nitric oxide under the same conditions are 4.5 and 59 percent at 400 mm. pressure; below 80 mm. no mixture is flammable (*343*).

The limits of carbon disulfide in any mixture of nitrous and nitric oxides, at 150 mm. pressure, can be read from curves in the original bulletin (*344*).

Limits of ignitibility by a weak spark (rather than limits of flammability as claimed) of carbon disulfide in nitric oxide and in nitrogen peroxide have been recorded (*8*).

CARBON OXYSULFIDE

The limits of carbon oxysulfide in air, observed, perhaps, in a eudiometer tube, were 11.9 and 28.5 percent (*150*).

CARBON MONOXIDE

CARBON MONOXIDE IN AIR

When a small spark was passed near the lower confines of a carbon monoxide-air mixture standing over water in a vessel 6 feet high and 12 inches square in section, the following observations were made (63):

12.3 and 12.33 percent carbon monoxide.—Stout ring of flame was formed, but flame did not travel the whole length of the vessel.

12.5 and 12.7 percent carbon monoxide.—A ring of flame first formed, then broke and filled the upper part of the vessel with striae of flame.

12.9 percent carbon monoxide.—A flame as wide as the vessel itself, with a strongly curved convex front, passed slowly and steadily up through the whole mixture.

In a wide space, therefore, it was concluded that the lower limit of carbon monoxide in air was 12.5 percent carbon monoxide.

The higher limit of flammability has not been determined in large vessels, but experiments in a wide, short vessel and in a long, narrow vessel have indicated (64) that the higher limit in a large volume is about 74.2 percent carbon monoxide.

The figures for both limits refer to gases saturated with water vapor at 18° to 19° C. When water vapor is removed as completely as is possible in laboratory experiments, the most explosive mixtures of carbon monoxide and oxygen can be ignited only by unusually powerful electric sparks, but passage over calcium chloride raises the lower limit of carbon monoxide in air, in a tube 2 inches in diameter, from 13.1 to 15.9 percent (70). Other experiments with roughly dried mixtures gave the limits 15.8 and 68.5 percent for a 2-inch-diameter tube, 14.5 and 68.4 percent for a 4-inch tube (33).

The limits with downward propagation of flame have not been determined in large vessels.

Observations in Small Vessels.—The lower limit with upward propagation observed in closed vessels rose somewhat as the diameter of the container was decreased; the limits were 12.8, 13.1, and 13.2 percent in 3-, 2-, and 1-inch tubes, respectively. The corresponding higher limits were 72, 72, and 71 percent (356).

Figure 10 indicates the limits with downward propagation in tubes of various diameters. The limits narrow rapidly when the diameter of the tube falls below 1 cm. and coincide when it is a little more than 2 mm.

The lower limit with horizontal propagation (356) in closed tubes is 15.9 percent CO for a tube 25 mm. in diameter, 14.1 percent CO for a 50-mm. tube, and 13.6 percent CO for a 75-mm.

tube. The limits for propagation throughout a closed 35-cc. globe with side ignition are 14.2 and 74.7 percent (297), and for propagation in a 350-cc. globe with ignition near the lowest point, 12.7 and 75.4 percent (368).

In round figures, therefore, the limits for carbon monoxide in air saturated with water vapor at laboratory temperature and pressure are 12.5 and 74 percent CO for upward propagation, 13.5 percent CO (lower limit) for horizontal propagation, and 15 and 71 percent CO for downward propagation. The figures for horizontal and downward propagation are based on observations in closed tubes in which the gases were under variable pressure during the experiment.

Influence of Pressure.—Figure 11 shows the limits of carbon monoxide in air under pressures greater than atmospheric (17, 18, 324). The effect of raising the initial temperature to 100° C. and of saturation with water vapor at 100° C. is shown for pressures of 32 and 64 atmospheres. The range of flammability of dry mixtures is narrowed by increase of pressure.

At higher pressures than those in figure 11 the range of flammability widens somewhat, until at 800 atmospheres the limits are 19.2 and 57 percent carbon monoxide (10).

Some old experiments below atmospheric pressure gave the following limiting pressures of flammability, with downward propagation of flame in several mixtures of carbon monoxide and air (220):

Limiting pressures for downward propagation of flame, carbon monoxide-air mixtures

Carbon monoxide, percent	Pressure at which flame was propagated, mm.	Pressure at which flame was not propagated, mm.
16.4	454	411
18.6	144	112
27.9	89	79
46.5 [1]	94	79

[1] The last mixture in this list could not be ignited at 76 mm. either by an induction-coil spark or by the flame of guncotton.

More recent experiments, made in a burette, indicated a small increase in the higher limit as the pressure was reduced (86).

Influence of Temperature.—Four sets of observations have been made (12, 220, 297, 358) on the influence of temperature. Probably the most reliable results are those (358) in table 10, determined in a closed tube 2.5 cm. in diameter and 150 cm. in length, with downward propagation of flame. These results are plotted in figure 12 with two older approximate values indicated by stars (220) that extend the lower limit results to nearly 600° C.
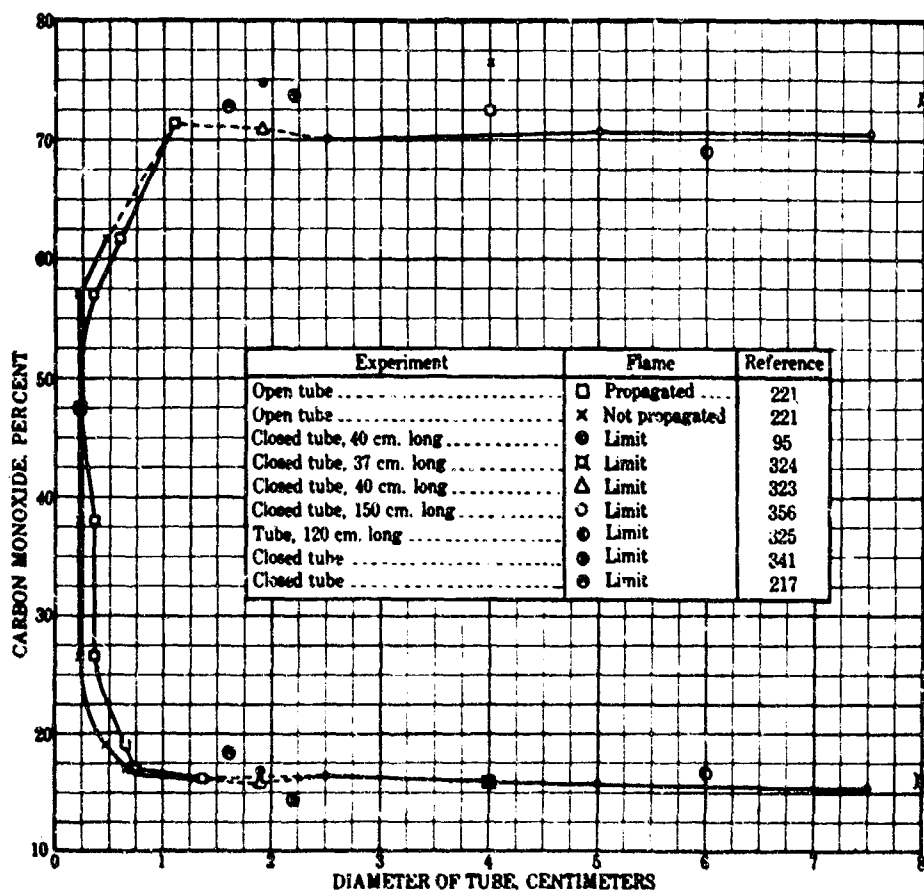
FIGURE 10.—Limits of Flammability of Carbon Monoxide in Air (Downward Propagation), Showing Effect of Diameter of Tube.

At 659° C. a 5.65-percent mixture was inflamed (*216*); at 727° an 82.9-percent mixture was inflamed (*288*).

TABLE 10.—*Influence of temperature on limits of flammability of carbon monoxide in air*

Temperature, ° C.	Limits of flammability of carbon monoxide, percent		Calculated flame temperatures, ° C.	
	Lower	Higher	Lower limit	Higher limit
17±3	16.3	70 0	1, 490	1, 120
50	15.7		1, 465	
100	14.8	71.5	1, 435	1, 130
150	14.2		1, 425	
200	13.5	73.0	1, 410	1, 160
240	12.0		1, 405	
300	12.4	75 0	1, 405	1, 170
350	12.0		1, 410	
400	11.4	77.5	1, 410	1, 175

The flame temperature necessary to propagate flame downward is much above the ignition temperature (650° C.) of a jet of carbon monoxide in air. It is remarkable that the calculated flame temperatures for the higher-limit mixtures should be so much lower than those for the lower limits; an ad hoc explanation is that the higher-limit mixtures react more rapidly than those of the lower limit, as the law of mass action points to most rapid reaction, at constant temperature, in the mixture that contains 66.7 percent carbon monoxide; but the difference in flame temperatures for the two limits seems too great to be thus explained.

The influence of temperature on the limits at high pressures is shown in figure 11.

Influence of Impurities.—The lower limit of carbon monoxide in air, with downward propagation of flame, was raised 3 percent by addition of iron carbonyl (0.028 cc. liquid vaporized per liter). The higher limit was reduced from 69 to about 43 percent by addition of iron carbonyl (0.022 cc. liquid vaporized per liter) (*325*).

The lower limit, with upward propagation of flame in a 2-inch-diameter tube, was not affected by the addition of 0.3 or 1.0 percent of nitric oxide (*70*).
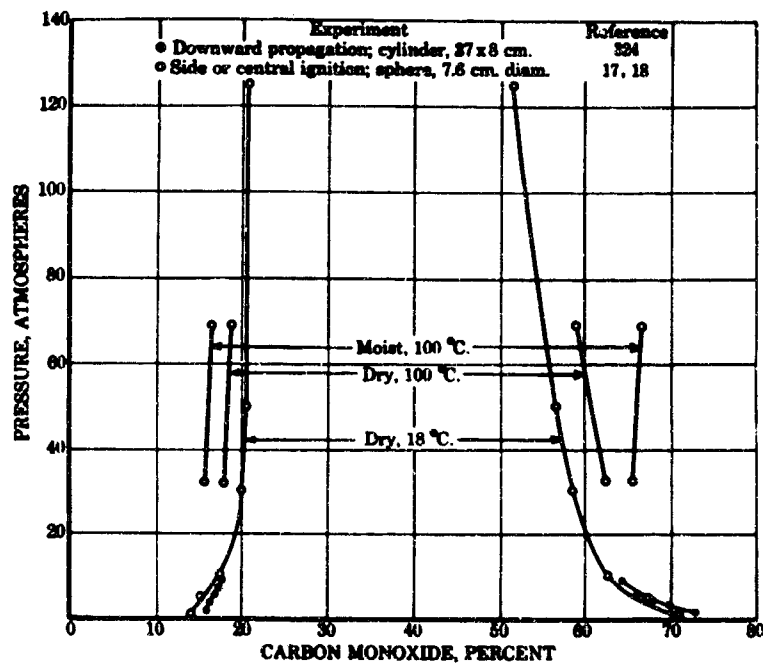
FIGURE 11.—Effect of Pressures Above Normal on Limits of Carbon Monoxide in Air.
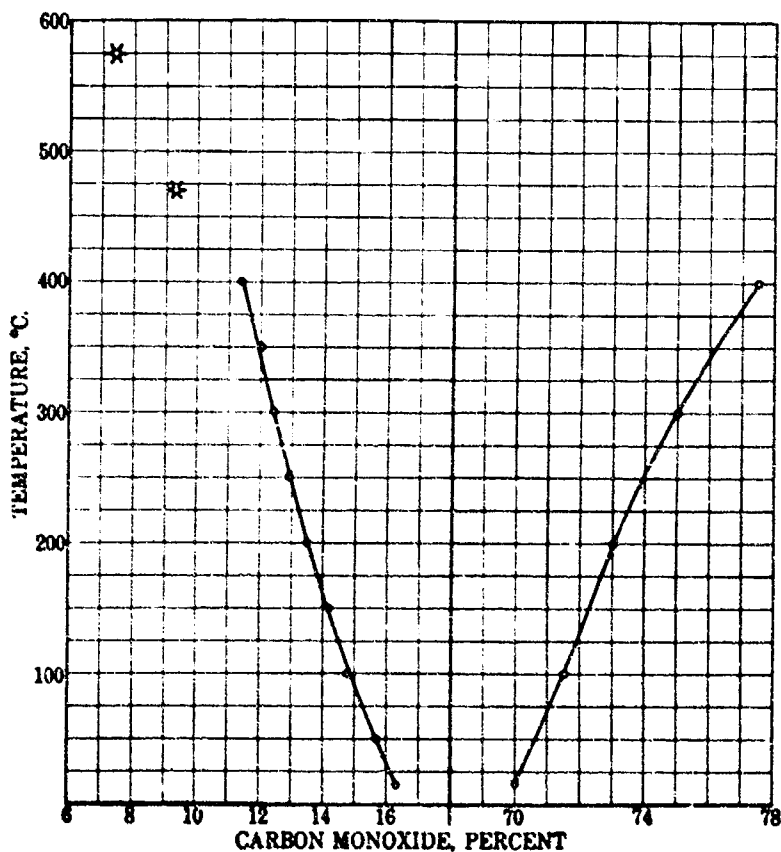
FIGURE 12.—Limits of Flammability of Carbon Monoxide in Air (Downward Propagation of Flame), Showing Influence of Temperature.

CARBON MONOXIDE IN OXYGEN

The second earliest recorded limits known to the present writers are those for carbon monoxide in oxygen. In 1810 John Dalton wrote "* * * unless the carbonic oxide amount to at least one-fifth of the mixture, it will not explode; and the oxygen must be at least one-fifteenth of the mixture" (76a).

The limits of carbon monoxide in oxygen, with downward propagation of flame in a Bunte burette 19 mm. in diameter, were 16.7 and 93.5 percent in nearly pure oxygen (323); in a closed tube 17 mm. in diameter, 16.7 and 93.9 percent (345). For propagation throughout a 35-cc. globe with side ignition the limits were 15.5 and 93.9 percent (297). Earlier observations are consistent with these figures, except that Wagner's low-limit figure was too high because he used a weak source of ignition (243, 346).

Influence of Pressure.—The limits were not appreciably narrowed until the pressure was reduced below 150 mm., when a moderately strong igniting spark was used. At lower pressures ignition becomes difficult to insure (65, 86).

Influence of Temperature.—In a 35-cc. closed bulb the limits were 15.5 and 93.9 percent at 15° C. and 14.2 and 95.3 at 200° C. (297).

CARBON MONOXIDE IN OTHER ATMOSPHERES

Atmospheres of Composition Between Air and Pure Oxygen.—With downward propagation of flame in a Bunte burette 1.9 cm. in diameter the lower limit rose gradually from 15.6 percent carbon monoxide in air to 16.7 percent in nearly pure oxygen. The higher limit rose from 70.9 percent carbon monoxide in air to 87.6 in a 51-percent oxygen mixture, 91 percent in a 71-percent oxygen mixture, and 93.5 percent in nearly pure oxygen (325).

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of flammability of carbon monoxide in all mixtures of air and nitrogen, or air from which part of the oxygen has been removed, are shown in figure 13. The determinations were made in a tube 6 feet in length and 2 inches in diameter, with upward propagation of flame from an open end (133). From the ordinates of the "nose" of this curve it may be calculated that no mixture of carbon
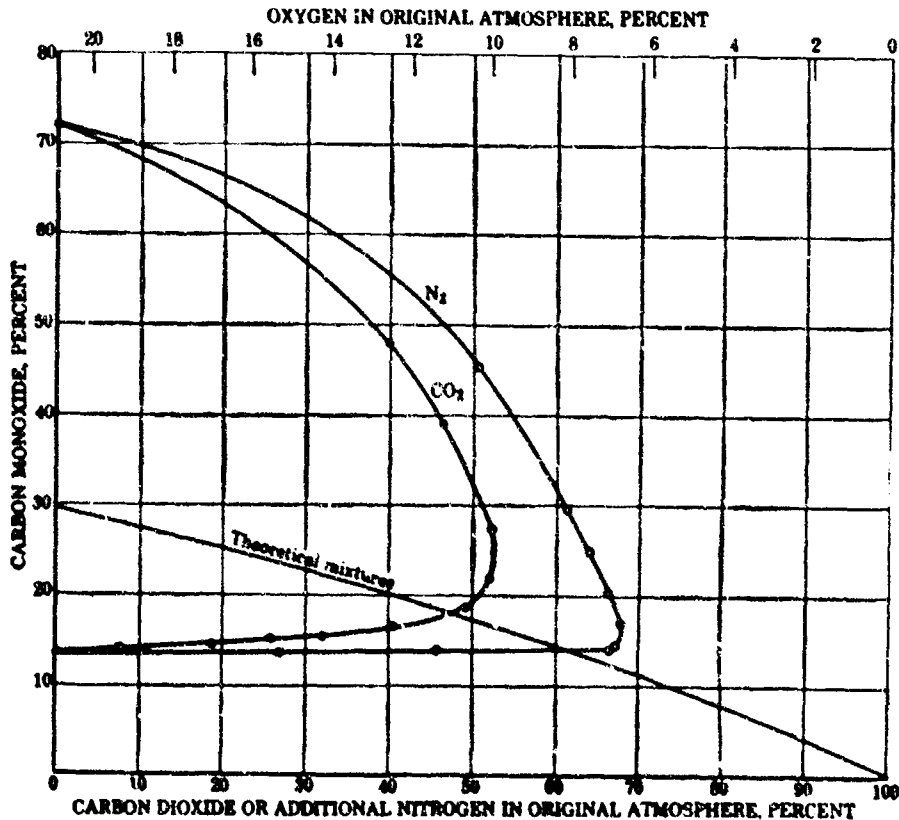
FIGURE 13.— Limits of Flammability of Carbon Monoxide in Air and Carbon Dioxide or Nitrogen.
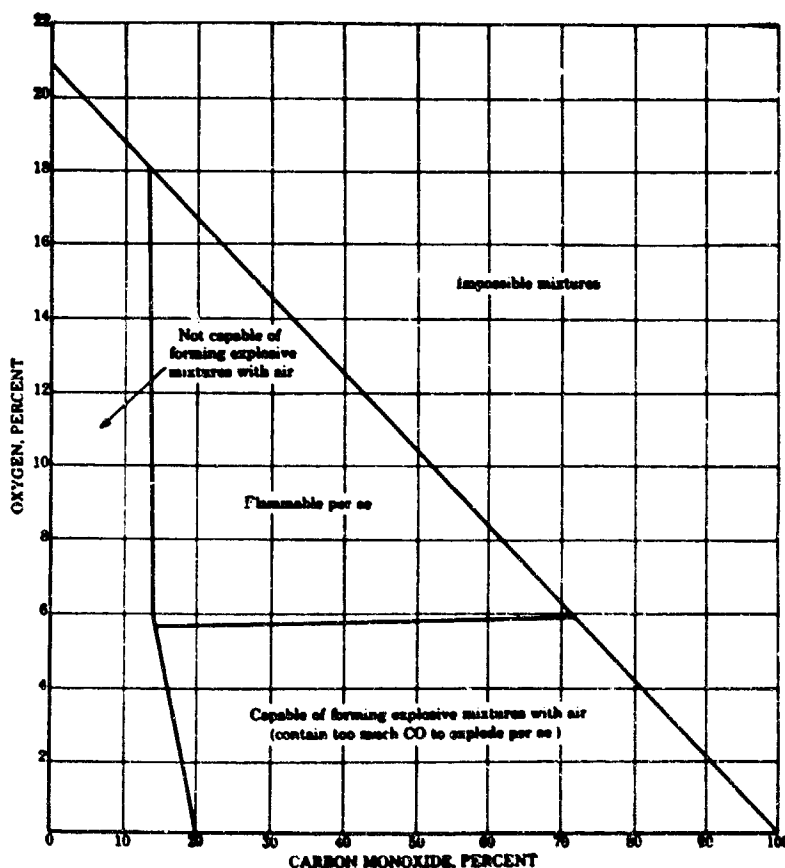
FIGURE 14.—Relation Between Quantitative Composition and Explosibility of Mixtures of Carbon Monoxide, Air, and Nitrogen.

monoxide, nitrogen, and air at atmospheric pressure and temperature is capable of propagating flame if it contains less than 5.6 percent oxygen (*167*).

For some purposes the results are more useful when expressed (*62*) as in figure 14. For example, a mixture that contains 20 percent carbon monoxide, 8 percent oxygen, and the remainder nitrogen is explosive. If the oxygen is reduced to 4 percent and the carbon monoxide remains at 20 percent, the mixture is no longer explosive but will become so on admixture with suitable amounts of air. If the carbon monoxide is less than 20 percent and oxygen is absent, no mixture with air is flammable.

In figure 14, "impossible mixtures" cannot be produced by mixing air, nitrogen, and carbon monoxide. For more detailed explanations compare the corresponding section on methane limits in mixtures of air and nitrogen.

The limits with downward propagation of flame in a closed tube 2.2 cm. in diameter have also been determined (*341*).

All Atmospheres of Oxygen and Nitrogen.— The limits of carbon monoxide in all mixtures of oxygen and nitrogen, with downward propagation of flame in tubes 1.5 and 1.7 cm. in diameter, are given in triangular diagrams (*228, 345*).

Atmospheres of Air and Water Vapor.—The limits of mixtures of carbon monoxide and air standing over water in a 350-cc. spherical vessel, and ignited near the water surface, have been determined at various temperatures. As the temperature rises, and consequently the water-vapor content also, the lower limit rises slowly and the higher limit falls rapidly, as with other diluents. When 54 percent of water vapor is present the limits coincide at about 18 percent carbon monoxide (*368*).

Earlier experiments, made in a Bunte burette, show similar effects, but the range of flammability is narrower (*95*).

Drying by calcium chloride has an appreciable effect on the lower limit of carbon monoxide in air (p. 31).

Atmospheres of Air and Carbon Dioxide.— The limits of flammability of carbon monoxide in all mixtures of air and carbon dioxide can be read from one of the curves in figure 13. The determinations were made in a tube 6 feet in length and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation *(133, 167)*.

Earlier observations *(95)* show, as might be expected, more rapid narrowing of the limits in Bunte burette experiments.

The limits with downward propagation in a closed tube 2.2 cm. in diameter have also been determined *(341)*.

Atmospheres of Air and Argon or Helium.— The limits of carbon monoxide in mixtures of air with argon and with helium, with downward propagation of flame in a closed tube 2.2 cm. in diameter, have been determined *(341)*.

Atmospheres of Air Mixed with Vapors of Halogenated Hydrocarbons.— The "theoretical" mixture of carbon monoxide and air (29.6 percent CO) was rendered nonflammable in a 4.4-cm.-diameter tube, open at the firing end, by (a) 2.05 percent of carbon tetrachloride for upward propagation of flame and (b) 1.16 percent for downward propagation. On reducing the percentage of nitrogen, more carbon tetrachloride was required, and on increasing it less was required, but the ratio of (a) to (b) remained constant *(91)*.

Series of results showing the lower and higher limits of carbon monoxide in air containing increasing amounts of the vapors of dichloroethylene and trichloroethylene have been reported; they were observed in small burettes 15 mm. in diameter, so have limited value *(199)*. Similar experiments have been made with the vapors of other halogen derivatives *(338)*.

The addition of increasing amounts of methyl bromide to the air causes the limits of carbon monoxide to approach and, in a 2-inch-diameter tube, to meet when 5.2 percent of the mixture is methyl bromide *(58)*. For a comment, compare the corresponding paragraph on hydrogen (p. 22).

Atmospheres in Which Nitrogen of the Air Is Replaced by Carbon Dioxide.— In a closed 35-cc. globe with side ignition the limits were 21.8 and 72.8 percent carbon monoxide in a mixture of 20.9 percent oxygen and 79.1 percent carbon dioxide compared with 14.2 and 74.7 percent, respectively, in air in the same apparatus *(297)*. Some earlier figures *(276)* may be regarded as supplanted by those just quoted. Results showing the influence of temperature on limits in this series are irregular.

Atmospheres of Oxygen and Carbon Dioxide and of Oxygen and Argon.— Limits in these atmospheres have been determined with down-

ward propagation of flame in a 1.7-cm.-diameter tube *(345)*.

Atmospheres of Oxygen and Chlorine.— The limits of carbon monoxide in mixtures of oxygen and chlorine, with downward propagation of flame in a tube 15 mm. in diameter, are plotted in a triangular diagram. No mixture of carbon monoxide and chlorine was flammable *(228)*.

Atmospheres of Nitrous and Nitric Oxides.— The limits of carbon monoxide in nitrous oxide, with downward propagation of flame in a 15-mm. burette, are 18.7 and 83.6 percent *(339)*, in nitric oxide (wrongly called nitrous oxide by the author—a Netherlands chemist writing in English), 30.9 and 48.4 percent *(228)*. The region of flammability of mixtures of carbon monoxide with mixtures of nitrous and nitric oxides has been plotted in a triangular diagram *(339)*, but the spark used was too weak to ignite any mixture of carbon monoxide and nitric oxide *(228)*.

Dilution of 2CO+O₂.— The following results were obtained with downward propagation of flame in diluted $2CO+O_2$ in a Bunte burette 19 mm. in diameter *(95)*:

Effect of diluents upon flammability of $2CO+O_2$

Diluent:	Percentage of $2CO+O_2$ which, with diluent, gives a mixture at limit of flammability.
Oxygen	23.4
Nitrogen	26.6
Carbon dioxide	35.3

Nitrogen evidently has a slightly greater extinctive action than oxygen, although it has less heat capacity; carbon dioxide, which has much greater heat capacity, also has a greater extinctive action.

CHLORINE

ATMOSPHERE OF FLUORINE

When a mixture of chlorine and fluorine was sparked in a small cylindrical tube, a yellowish-red flame spread through the tube, accompanied by an explosion when the proportions of the gases were suitable. On drying the gases and apparatus completely no reaction occurred, but on admitting moisture, flame and explosion were once more obtained *(108)*. Although the limits were not obtained in these experiments, they show that chlorine and fluorine form flammable mixtures under certain conditions.

CHLORINE MONOXIDE

ATMOSPHERE OF OXYGEN

All mixtures of chlorine monoxide and oxygen containing more than 23.5 percent of the former are capable of propagating flame upward when "ignited" by a spark in a tube 3.4 cm. in diameter and 90 cm. in length *(78)*.

METHANE

METHANE IN AIR

When a spark was passed near the lower confines of methane-air mixtures standing over water in a vessel 6 feet high and 12 inches square in section, the following observations were made (63):

5.1 percent methane.—A vortex ring of flame traveled upward about 12 inches, broke, and died out as a tongue of flame about 12 inches higher.

5.3 percent methane.—In one experiment the ring of flame resolved itself into a flame that traveled steadily to the top of the vessel; in other experiments the flame became extinguished during a violent uprush on one side.

5.6 percent methane.—A steady flame with a convex front passed throughout the mixture.

These experiments have been repeated with a glass cylinder 7 feet in height and 10 inches in diameter. The limit observed was 5.32 percent methane. Steady conditions were obtained more easily in the 10-inch tube than in the box (68).

Independent observers conducted experiments in a vessel similar to that first described, which led them to conclude that the lower limit for inflammation upward was about 4.9 percent methane (45). Comparison of the two sets of experiments shows, however, that they were conducted differently. In each set the gas was ignited electrically at the lower end of the vessel; in the first set the flame traveled toward the closed end with a release behind the flame, but in the second set the flame traveled from the closed end toward a paper diaphragm that "upon ignition broke and gave a vent for the burned gases." The authors have repeated both sets of experiments and confirmed both results: the figures obtained were 5.28 percent for propagation upward away from the open end and 5.01 percent for upward propagation in the same vessel toward the open end. However, there was a great difference between the appearance of the limit flames in the two tests. In the first they appeared, after traveling about 12 inches, to be spreading from side to side of the vessel with a strongly convex front and to travel at uniform speed; in the second the flame was apparently not continuous from side to side but consisted of innumerable vertical streaks of flame, traveling much faster and evidently in a turbulent mixture. It was difficult to be sure that the latter flame could travel indefinitely and not be extinguished. In the former experiments the flame traveled into quiescent gas; in the latter the flame traveled into gas that had considerable motion on account of upward expansion of the heated gas.

Hence, the conclusion is that, in a wide space, the lower limit of methane in air saturated with water vapor at laboratory temperature is 5.3 percent methane, but that, if the flame is traveling upward from the closed to the open end of a vessel in gas which is therefore in motion, it may travel at least 6 feet when the proportion of methane is not less than 5 percent. Furthermore, in certain circumstances "the flames of mixtures containing 5.3 to 5.6 percent of methane are very sensitive to extinction by shock" (63).

The higher limit of methane in air saturated with water vapor has been determined in a glass tube 7 feet in length and 10 inches in diameter to be 13.87 percent methane (68). This figure may be taken as correcting an earlier and higher estimate (64) based on observations in short, wide vessels and long, narrow vessels.

In a similar vessel with a paper release at the top equivalent to an open end, the higher limit was 15.2 percent under the condition of movement imparted to the gases (45).

Downward Propagation of Flame.—In a large box nearly 6 feet long and 12 inches square in section the limits with downward propagation of flame in a quiescent mixture were 5.75 and 13.6 percent methane; when the box was closed at the top and open at the bottom, so that motion was imparted to the mixture by the expansion on burning, the lower limit with downward propagation was 5.45 percent (45).

Horizontal Propagation of Flame.—In the same box the lower limit with horizontal propagation was 5.55 percent methane. The position of the open end, whether behind or ahead of the flame, was not stated (45).

In a horizontal glass cylinder 7 feet in length and 10 inches in diameter the limits with propagation throughout the length of the tube from open to closed end were 5.42 to 14.03 percent methane. The mixtures were only partly saturated with water vapor; if completely saturated, the higher limit would be reduced somewhat, probably to a value not exceeding 13.87 percent methane—that with upward propagation in the same vessel (68).

Observations in Small Vessels.—Numerous observations have been made of the limits of methane in small vessels. On the whole, the results are fairly consistent, as shown by tables 11 to 14 when allowance is made for variation in experimental conditions. Outstanding discrepant figures are not quoted here, because they have been explained as due to faulty experiment or faulty interpretation. For example, in at least one research it is certain that the mixtures of methane and air were not homogeneous; in another (278) the observation of a small pressure change on sparking was erroneously interpreted as an indication of

flammability; in a third (232) the flame speeds in a series of flammable mixtures of methane and air were extrapolated to zero speed, the corresponding composition being taken as the limit of flammability—an error, because a "limit" mixture has a flame speed that is far from zero. Many of the older figures are omitted because they are but rough approximations compared with more recent results, with which, however, they are not at variance.

A recent series of experiments in narrow tubes has, however, given some anomalous results, not yet explained. In a 2-cm.-diameter tube 60 cm. long, the limits were normally 5.40 and 13.72 percent; but, after the tube had been cleaned with chromic acid, washed, dried, and evacuated to 0.001 mm., the limits observed were 4.70 and 12.86 percent. An extended series of experiments was then made with a "natural gas" containing 94 percent of methane and 0.5 percent of "various hydrocarbons." Tubes 2.5, 2.0, 1.5, and 1.0 cm. in diameter were used, and both limits were determined for upward and downward propagation of flame. The "clean-tube" limits were always lower than the corresponding "normal-tube" limits, the difference being independent of tube diameter

for both limits (downward propagation) and for the higher limit (upward propagation). It is difficult to explain a "wall effect" that is independent of tube diameter (264).

Upward Propagation in Small Vessels.—Table 11 shows the limits with upward propagation of flame in mixtures of methane and air in the smaller vessels. It is evident that the limits found in wide vessels open behind the flame--5.3 and 13.87 for gases saturated with water vapor—are not appreciably narrower in open tubes 5 cm. in diameter. In closed tubes, however, the higher limit is greater than in open tubes of equal diameter. This is explained by the observation that increase of pressure raises the higher limit; enough pressure to affect the limit is developed in closed tubes in the earlier stages of propagation, while the flame is still assisted by the initial impulse from the source of ignition. This explanation is confirmed by a comparison of two experiments in tubes of the same diameter (5 cm.) but of very different lengths. The shorter tube gave a greater higher-limit figure than the longer tube, because the pressure must rise faster and to a greater quantity in the shorter tube.

TABLE 11.—*Limits of flammability of methane in air, with upward propagation of flame in tubes*

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
10.2	96	Closed	5.00	15.00	Dry	142
7.5	150	...do	5.35	14.85	Half-saturated	356
6.2	33	Open	5.45	13.5	Saturated	95
6.0	200	Closed	5.40	14.8	Small	33
5.3	150	Open	5.26	14.3	Dry	93
5.0	50	Closed		15.11		277
5.0	150	Open	5.40	14.25	Half-saturated	356
5.0	180	...do	5.24	14.02	Dry	63
5.0	180	...do	5.33	13.80	Saturated	69
4.7	100	...do	5.3	14.3	Small	269
4.0	100	Closed	5.5	14.1		219
2.7		Open	5.28		Dry	225
2.5	150	...do	5.5		Saturated	271
2.5	150	Closed	5.80	13.20	Half-saturated	356
2.25	125	Open	5.48		Nearly dry	110

Horizontal Propagation in Small Vessels.—Table 12 shows the limits with horizontal propagation in the smaller vessels. The limits for closed tubes are narrowed appreciably by reducing the diameter of the tube to 2.5 cm. In open tubes the limits meet when the diameter of the tube is reduced to 0.45 cm. Flame is not propagated, except for a short distance from the source of ignition, along a tube 0.36 cm. in diameter.

Downward Propagation in Small Vessels.—Table 13 shows the limits with downward propagation of flame in the smaller vessels. The limits throughout are somewhat narrower than those found in the largest vessel for the same direction of propagation.

Propagation in Spherical Vessels.—Table 14 shows the limits for propagation of flame throughout mixtures of methane and air in closed spherical vessels of various sizes. The

TABLE 12.—*Limits of flammability of methane in air with horizontal propagation of flame in tubes*

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed	5.40	13.95	Half-saturated	356
6.0	200	do	5.4	14.3	Small	33
5.0	150	do	5.65	13.95	Half-saturated	356
5.0	50	do	5.39	14.28		277
4.0	100	do	5.6	13.9		210
2.7		Open	5.64		Dry	225
2.5	150	do	5.85	13.3	Saturated	271
2.5	150	Closed	6.20	12.90	Half-saturated	356
2.25	125	Open	6.04		Nearly dry	110
2.0	40	Closed	5.59	13.31		277
.90	300	Open	7.8	11.6	Saturated	276
.81	300	do	8.3	10.9	do	276
.72	300	do	8.4	10.6	do	276
.56	300	do	8.4	10.6	do	276
.45	300	do	[1] 9.95		do	276
.36	300	do	Nil.		do	276

[1] Limits coincide at this composition.

TABLE 13.—*Limits of flammability of methane in air, with downward propagation of flame in tubes*

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
8.0	37	Closed	5.9	12.9	Saturated	324
7.5	150	do	5.95	13.35	Half-saturated	356
6.2	33	Open	6.3		Saturated	95
6.1	120		6.1	13.0	Partly dry	325
6.0	200	Closed	6.0	13.1	Small	33
5.0	50	do	5.80	13.38		277
5.0	150	do	6.12	13.25	Half-saturated	356
5.0	125	Open	5.85		Dry	70
4.0	100	Closed	6.1	13.3		210
2.7		Open	5.84		Dry	225
2.5	150	do	6.1		Saturated	271
2.5	150	Closed	6.22	12.80	Half-saturated	356
2.25	125	Open	6.41		Nearly dry	110
2.2		Closed	5.6	13.6		541
1.9	40	do	6.1	12.8	Saturated	95
1.9	40	do	6.15	12.0	do	323
.815		Open	6.25		Dry	225
.515		do	7.03		do	225

limits become somewhat narrower as the size of container is decreased and generally correspond more nearly with the limits for downward propagation in tubes than with those for either horizontal or upward propagation.

All Directions of Flame.—Figure 15 shows the lower limits of methane in a tube 2.25 cm. in diameter and 125 cm. in length, open at the firing end and inclined at various angles. As the direction of flame is changed from vertically upward to vertically downward, the increase in the lower limit is proportional to the change of angle over the range 90° to about 50° and to the change in sine of the angle from 50° to —90° (110).

TABLE 14.—*Limits of flammability of methane in air, in spherical vessels*

Capacity of vessel, cc	Point of ignition	Limits, percent		Content of aqueous vapor	Reference No.
		Lower	Higher		
2 800	Central	5.77		Saturated	957
2 000	do	5.6	14.8	Dry	32,33
100	Above	5.5	14.0		44
35	Side	6.0	12.5	Dry	897
35	do	5.9	13.1	Saturated	897
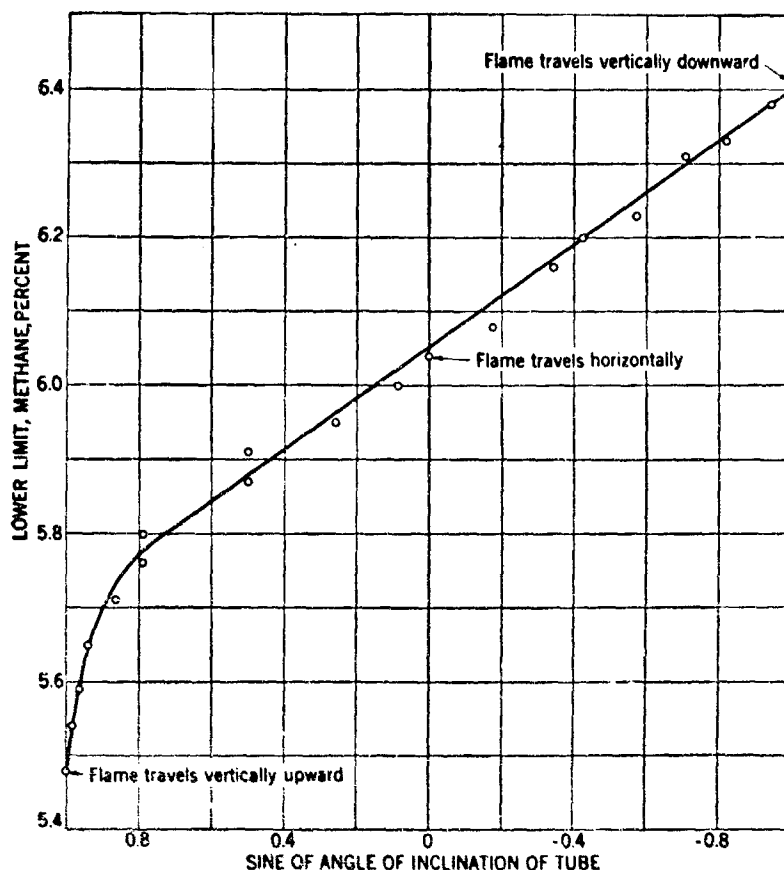
FIGURE 15.—Lower Limit of Methane for Various Directions of Propagation of Flame in a Tube 2.25 Cm. in Diameter.

Influence of Turbulence and Streaming Movement on Limits of Flammability.— When a small fan was rotated rapidly enough but not too rapidly in methane-air mixtures contained in a 4-liter globe, the lower limit of methane was 5.0 percent compared with 5.6 percent observed for quiescent mixtures in the same vessel. If the turbulence was too violent, however, even a 5.6-percent mixture did not propagate more than a short tongue of flame (33, 350).

A streaming movement of the gas mixture produces similar effects on the lower limit. At a speed of 35 to 65 cm. a second (69 to 128 feet a minute) flame was propagated in a 5.02-percent methane-air mixture but not at any speed in a 5.00-percent mixture (236). Hence, under appropriate conditions of movement of the gas mixture, the lower limit of methane is 5.0 percent. The same figure was obtained when movement of the mixture was produced by expansion caused by its own combustion in experiments on the propagation of flame from closed to open end of a large vessel (p. 137).

Reference may be made to observations of the effect of turbulence, in somewhat different cir-

cumstances, on the lower limit of natural gas in air (p. 115).

Influence of Pressure.—No measurable change in the limits of methane in air could be discovered, either when the pressure was varied between 753 and 794 mm. (225) or, in the lower limit for upward propagation of flame, when the pressure was varied from 1 to 2.9 atmospheres in a vessel of 11.3 liters capacity (211).

An interesting comparison has been made of the effect of change in pressure from 1 to 6 atmospheres on the limits with downward and horizontal propagation in tubes 2 cm. in diameter (235, 277). With downward propagation, the limits change steadily from 6.00 and 13.00 percent at 1 atmosphere to 6.40 and 14.05 percent at about 6 atmospheres. With horizontal propagation, the lower limit remained nearly constant (5.6 percent) over this range of pressure; the higher limit rose steadily from 13.31 percent at 1 atmosphere to 16.12 percent at about 6.5 atmospheres. In these experiments, therefore, the lower limit with horizontal propagation was unchanged, but that with downward propagation increased

steadily with increasing pressure. The higher limit with horizontal propagation increased more rapidly than that with downward propagation. (For an interpretation *see*, p. 4).

The limits observed under very high pressures (*14, 17, 324*) are shown in figure 16. One series of higher limits (*51*) is omitted, because it starts with too low a figure (10.65 percent) for 1 atmosphere pressure. The rapid increase in the higher limit is remarkable. The differences in the three series of results are to be ascribed to differences in experimental method and interpretation. Experiments almost of necessity had to be conducted in small vessels, but the results doubtless are a fair indication of the possibilities of explosion in larger vessels holding mixtures of compressed gases.

Figure 17 shows limits at less than atmospheric pressure and at various temperatures, in a tube 2 cm. in diameter and 50 cm. in length, with downward propagation of flame (*235*). The curve for 20° C. shows much wider limits at low pressures and extends to much lower pressures than those observed in an older series of tests (*47*). The more recent results were obtained with a stronger igniting spark; sparks that will ignite a flammable mixture at normal pressures may be much too weak to ignite it at low pressures.

Experiments in a wider tube, 5 cm. in diameter and 50 cm. in length, compare the limits for different directions of propagation of flame at pressures less than atmospheric (*277*). The curves for these limits are plotted in figure 18. Data were not obtained for upward propagation at the lower limit because, in the rather short vessel used, the issue was confused by the large "caps" of flame above the igniting spark. A complete curve for horizontal propagation in a tube 1.5 cm. in diameter and 120 cm. in length has, however, been obtained (*125*). It shows a small abnormality on the higher-limit side at 150 to 200 mm. pressure, where "green flames" were observed. A complete curve for propagation in a burette has also been obtained (*86*). Other curves for propagation in narrow tubes show abnormalities on either the lower- or higher-limit side at reduced pressures (*99*).

Influence of Temperature.—Several older observations have been criticized unfavorably on the grounds that the mixture underwent partial combustion in the heated experimental vessel before it was tested and its composition was thereby altered enough to affect the results. The less exceptionable results are compared in figure 19, which shows lower and higher limits up to temperatures at which spontaneous inflammation of the mixture was almost instan-
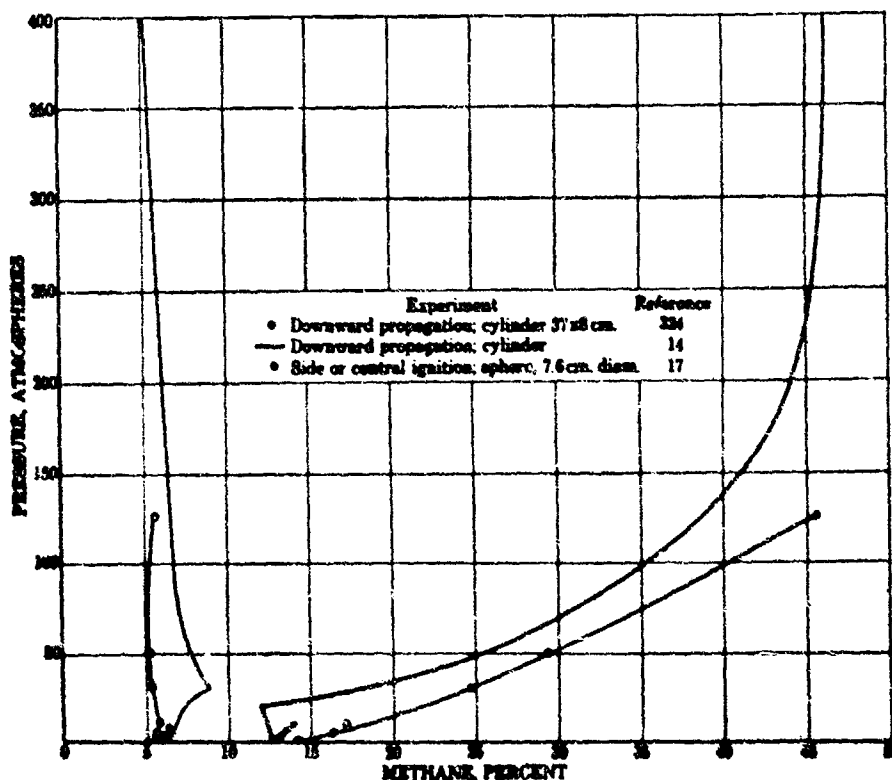
FIGURE 16.—Effect of Pressures Above Normal on Limits of Methane in Air.
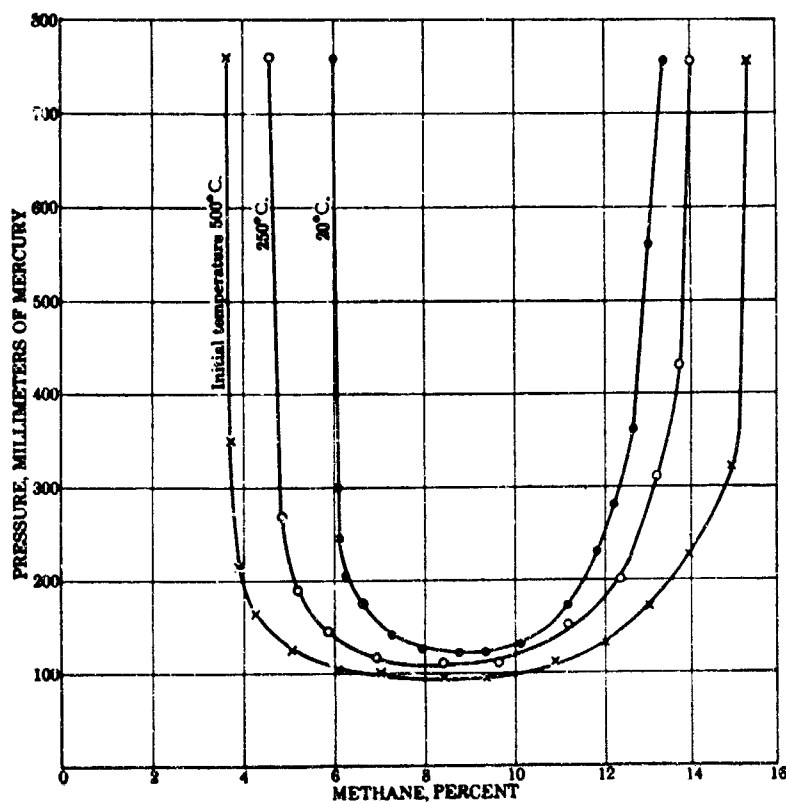
FIGURE 17.—Limits of Flammability of Methane in Air (Downward Propagation), Showing Influence of Pressure (Below Normal) and Temperature.
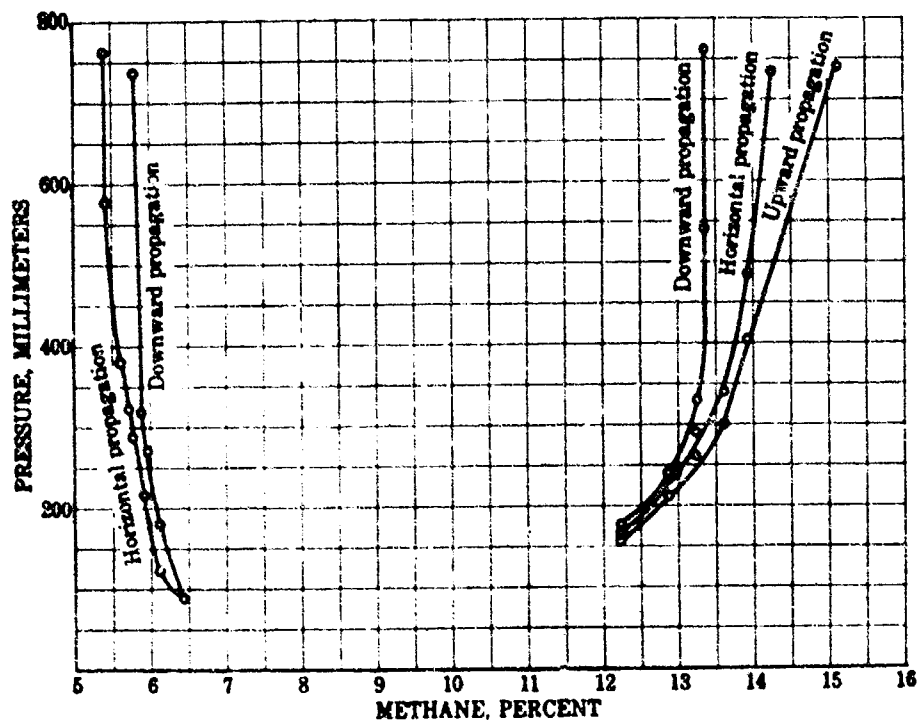
FIGURE 18.—Limits of Flammability of Methane in Air, Showing Influence of Pressure and of Direction of Propagation of Flame.
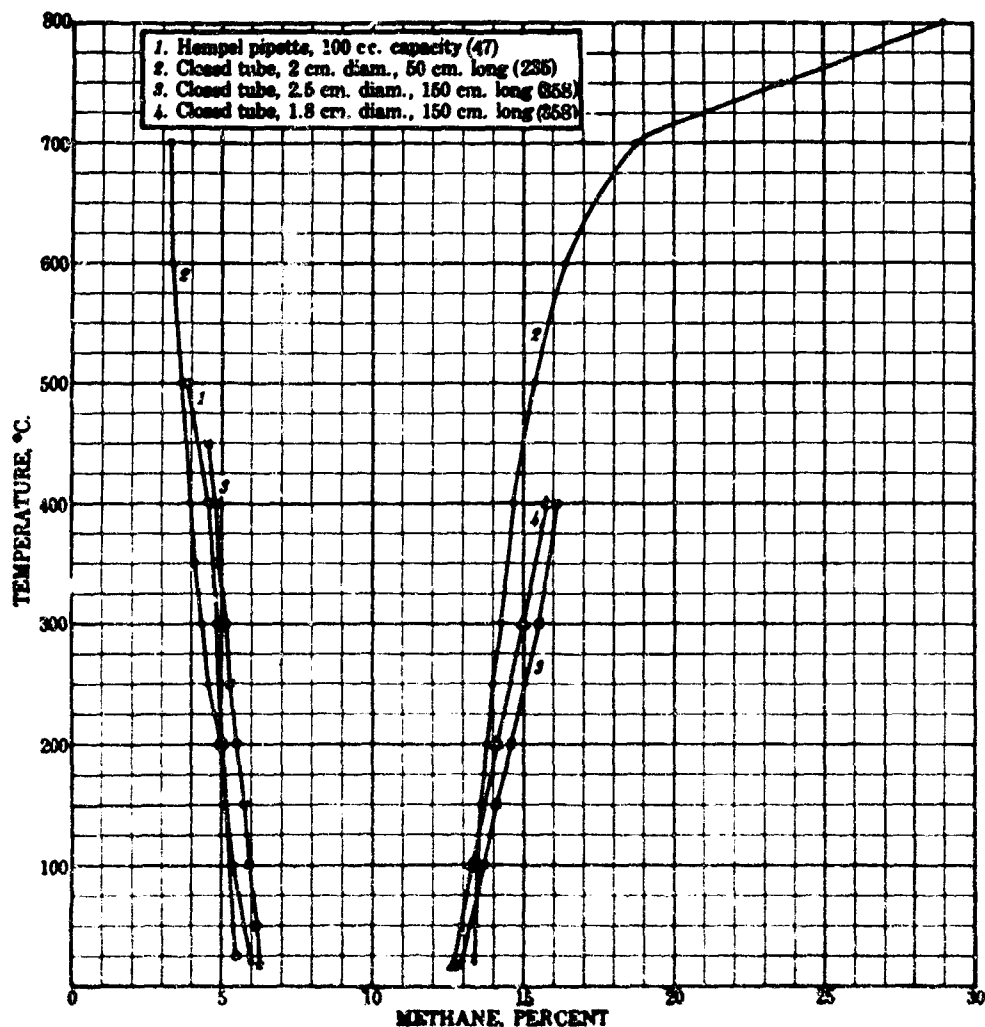
FIGURE 19.—Limits of Flammability of Methane in Air (Downward Propagation), Showing Influence of Temperature.

taneous. In each series the direction of propagation of flame was downward; the other conditions are indicated on the figure, together with the reference numbers. As will be noted, the range of flammability is widened considerably at both limits by increase of temperature, but ordinary variations of atmospheric temperature have an insignificant effect.[6]

Figure 17 shows the temperature effect at pressures less than normal.

The differences between the results of the several sets of tests in figure 19, although small for lower limits and not very large for higher limits, are real and must be due to the use of different apparatus. For higher limits the length of tube used seems to be the determining

factor, as shown by series 2 and 4 (fig. 19) with tubes of nearly the same diameter. Hence all the results are relative to the apparatus used and do not show the influence of temperature on limits defined as a property of the gas mixture alone. The results may, however, be taken as an indication of the effect of temperature on the true limits.

An unconfirmed observation is that, although the limits in moist methane-air mixtures are widened by increase in temperature, the lower limit as well as the higher limit is much raised by increase of temperature when the mixtures are dried with phosphorus pentoxide (297).

Low Temperatures.—At the temperature of liquid air the lower limit of methane with downward propagation of flame in a tube 2.5 cm. in diameter and 40 cm. in length, open at the firing end, is 7.5 ± 0.3 percent (170). In

---

[6] Formulas to express the influence of temperature on the limits have been given [?] for the range 0 to 400° C. thus for lower limit, $n = n_0 - 0.0812t$; for higher limit, $n = n_0 + 0.0224t$.

the same circumstances, but at room temperature, the limit is 6.1 percent.

Influence of Pressure at Various Temperatures.—The curves of figure 17 show the limits of flammability of methane-air mixtures at 20°, 250°, and 500° C. at all pressures below atmospheric. The limits were observed in a closed tube 2 cm. in diameter and 50 cm. in length (*235*).

A mixture of 2.1 percent methane in air was ignited by sudden compression to 80 atmospheres pressure, which produced a temperature of 705° C., and a mixture of 55 percent methane at 118 atmospheres and 540° C. (*87*).

Influence of Impurities.—The lower limit of methane in air, with downward propagation of flame, was raised about 1.3 percent by iron carbonyl (0.03 cc. liquid vaporized per liter). The higher limit was reduced from 13.0 to 10.5 percent by the same quantity of iron carbonyl (*325*).

METHANE IN OXYGEN

The limits of methane in oxygen, with upward propagation of flame in a 2-inch-diameter tube open at its lower end, are 5.15 and 60.5 percent (*138*).

Table 15 gives other determinations of the observed limits of methane in oxygen.

TABLE 15.—*Summary of other determinations of limits of flammability of methane in oxygen*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Reference No.
Diameter	Length		Lower	Higher	
2.5	150	Open.		5.4	*72*

Horizontal Propagation of Flame

2.5	150	Open	5.5	58.5	*72*

Downward Propagation of Flame

2.5	150	Open		6.3	*72*
20.0	2.2	Closed		54	*1.3*
1.9		do	6.1		*96*
1.9		do	5.45		*122*
1.7		do	5.6	57.1	*45*
		do		54	*1.3*

Propagation of Flame in Globe or Bomb

2.5 liters capacity	Closed	6.0		*97*
35 cc. capacity	do		57.0	*97*
30 cc. capacity	do		54.5	*44*

Influence of Pressure.—The limits of methane in oxygen were not appreciably narrowed until the pressure was reduced below 150 mm. A moderately strong igniting spark was used

(*65*). With a stronger spark the limits did not coincide until the pressure was reduced to 10 mm. (*80*). A curve has been obtained for results in a burette (*86*).

The higher limit is increased by an increase of pressure above atmospheric. One observation (*330*), incidental to other work, is that, at 10 atmospheres pressure, a mixture containing 71 percent methane slowly propagated flame. In a small bomb (*58*) the higher limit rose rapidly from 58.4 percent at 1 atmosphere to 81.7 percent at 60 atmospheres, then slowly to 84 percent at about 145 atmospheres; however, the mixtures contained about 4.5 percent nitrogen, and the limits would be somewhat higher in pure oxygen. Combustion was far from complete in such mixtures under moderately high pressure.

Influence of Temperature.—In a 35-cc. closed bulb the limits were 6.2 and 57.1 at 15° C. and 5.1 and 57.8 at 300° C. (*297*).

Influence of Temperature at High Pressures.—As the temperature is raised, the pressure required to make certain mixtures of methane and oxygen flammable decreases. For example, the pressure limit of a mixture containing 81.7 percent methane at atmospheric temperature was 60 atmospheres, but at 332° C. it was only about 24 atmospheres (*58*). Curves that show the higher limit at elevated temperatures and pressures are given in the original paper.

METHANE IN OTHER ATMOSPHERES

Atmospheres of Composition Between Air and Pure Oxygen.—The limits of methane in mixtures of nitrogen and oxygen richer in oxygen than ordinary air have been found as follows: (1) In a closed globe 2.5 liters in capacity the lower limit rose regularly from 5.8 percent in air to 6.0 percent in oxygen (*267*); (2) in a horizontal glass tube 2.5 cm. in diameter, open at the firing end, the lower limit fell from 5.8 percent in air to 5.7 percent in oxygen, and the higher limit rose linearly from 13.3 in air to 59.2 in oxygen (*189*); (3) in a closed tube 1.9 cm. in diameter the lower limit with downward propagation of flame rose regularly from 6.15 percent in air to 6.45 percent in oxygen. The higher limit rose from 12 percent in air to 38 percent in a 62-percent oxygen mixture and 52 percent in a 95-percent oxygen mixture (*325*).

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—Large-scale experiments with mixtures of methane, air, and nitrogen have been made in a tube 7 feet in length and 10 inches in diameter, with upward propagation of flame from the open end of the tube; the mixtures throughout were at atmospheric pressure and were saturated with water vapor. The range of observations shown in figure 20
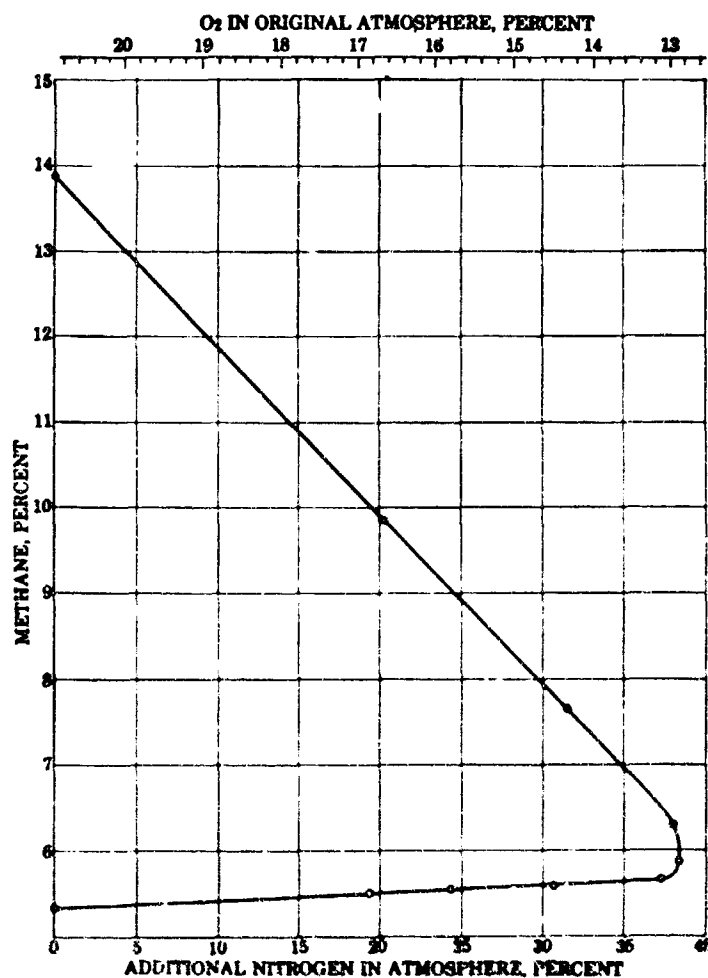
FIGURE 20.—Limits of Flammability of Methane in Mixtures of Air and Nitrogen (Experiments in Large Vessels).

covers all compositions from air to mixtures in which the amount of oxygen is too small for flame propagation, regardless of the amount of methane present. The abscissas represent the "atmosphere" in each mixture of air and nitrogen; for example, 25 percent "additional nitrogen" means that the "atmosphere" used for the observations was composed of 75 percent air and 25 percent nitrogen. Along the top of the diagram the corresponding percentages of oxygen in the atmosphere may be read. It is evident that no mixture of methane is flammable at ordinary temperatures and pressures when the atmosphere contains less than 12.8 percent oxygen and the remainder is nitrogen (68).

The results of observations made in smaller apparatus are shown in figure 21. In a 5-cm. tube, with upward propagation of flame in a dry mixture, the limits nearly coincide with those plotted in figure 20. The three curves

that show narrower limits represent experiments in various types of apparatus with downward propagation of flame. One curve shows greater values over part of the higher-limit range; the values were obtained in a closed vessel in which the pressure rose considerably during the inflammation, and increase of pressure is known to increase markedly the higher limit of methane. The limits of these mixtures with downward propagation of flame in a closed tube 2.2 cm. in diameter (54) and in a closed glass bulb 6.5 cm. in diameter (269) have also been determined.

For some purposes the results are more useful when expressed (62) as in figure 22. For example, it cannot be deduced from figure 20 without calculations, that the mixture

	Percent
Methane	12
Oxygen	2
Nitrogen	86

cannot form an explosive mixture with air, whatever the proportions used, whereas the mixture

	Percent
Methane	9
Oxygen	12
Nitrogen	79

although not itself explosive, may form a series of explosive mixtures with air. Figure 22 gives this information at a glance.

Explanation of Figure 23.—Figure 23 explains figure 22. The straight line *AD* (fig. 23) represents the composition of all mixtures of methane and pure air that contain up to 20 percent methane. No mixture of methane and air can fall above this line, and all mixtures of methane,

air, and nitrogen must fall below it. The line *BE* is the line of lower limits of flammability of methane and *CE* the line of higher limits. As the oxygen content falls, *BE* and *CE* approach each other until they meet at *E*. No mixture which contains less oxygen than that corresponding with *E* is explosive per se, but all mixtures in the area *BEC* are within the limits of flammability and are therefore explosive.

Next consider any mixture to the right of the line *CEF*; for example, the mixture represented by the point *G*. Join *GA*. Then *GA* represents the mixtures formed, in succession, as *G* is diluted with air. Because *GA* passes through the area *BEC* the mixture, as it is diluted with air, becomes explosive and remains so as long

O₂ IN ORIGINAL ATMOSPHERE, PERCENT

1. Hempel pipette, 100 c.c. capacity 5C
2. Tube, 2.7 cm. diam. 226
3. Bomb, 2.6 liters capacity 54
4. Sphere, 2 liters capacity 32
5. Tube, 5.0 cm. diam., upward propagation 60

ADDITIONAL NITROGEN IN ORIGINAL ATMOSPHERE, PERCENT
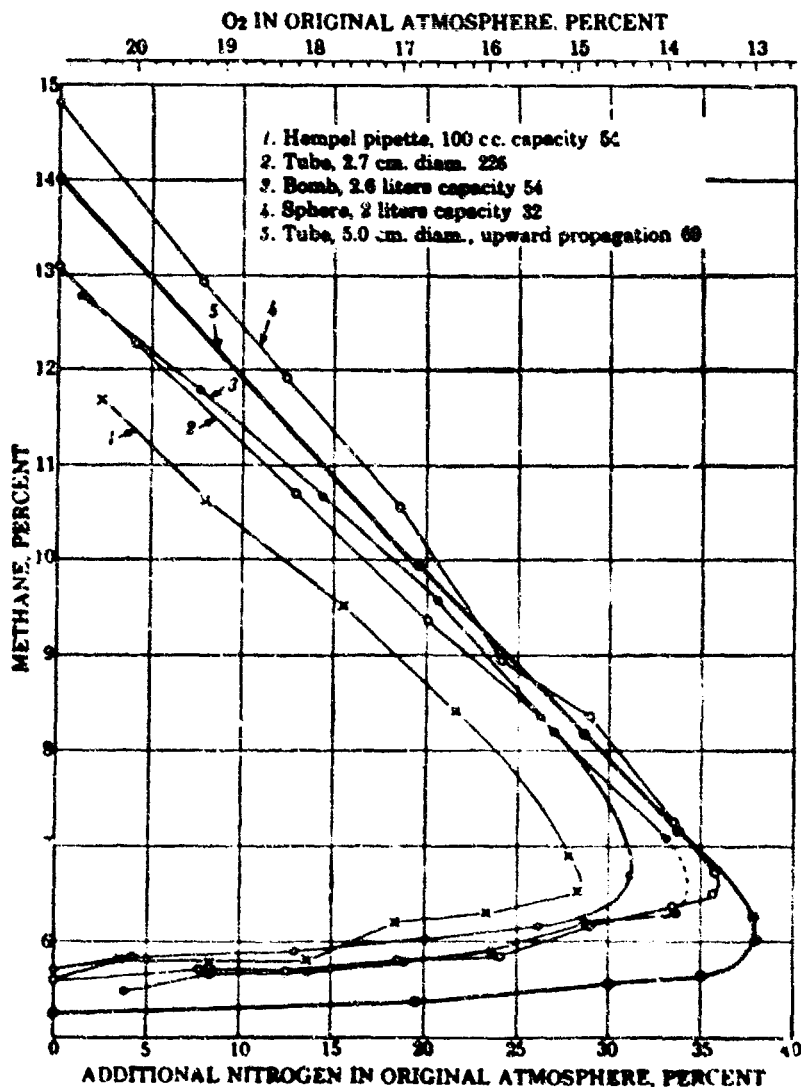
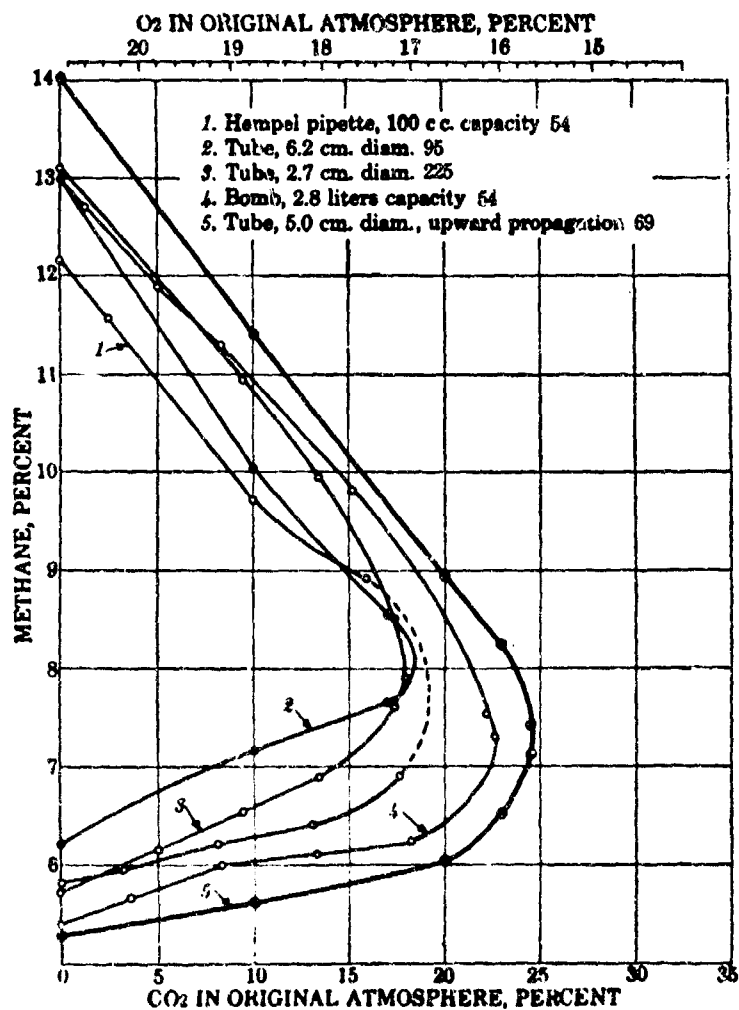FIGURE 21.—Limits of Flammability of Methane in Mixtures of Air and Nitrogen: Comparison of Results Obtained in Smaller Vessels.

22

20
Mixtures wh. h can not be
produced from methane and air

18

Flammable per se

16

14

12
Capable of forming flammable mixtures with air
(contain to much methane to explode per se)

OXYGEN, PERCENT

10

8
Not capable of
forming flammable
mixtures with air

6

4

2

0   2   4   6   8   10   12   14   16   18   20
METHANE, PERCENT
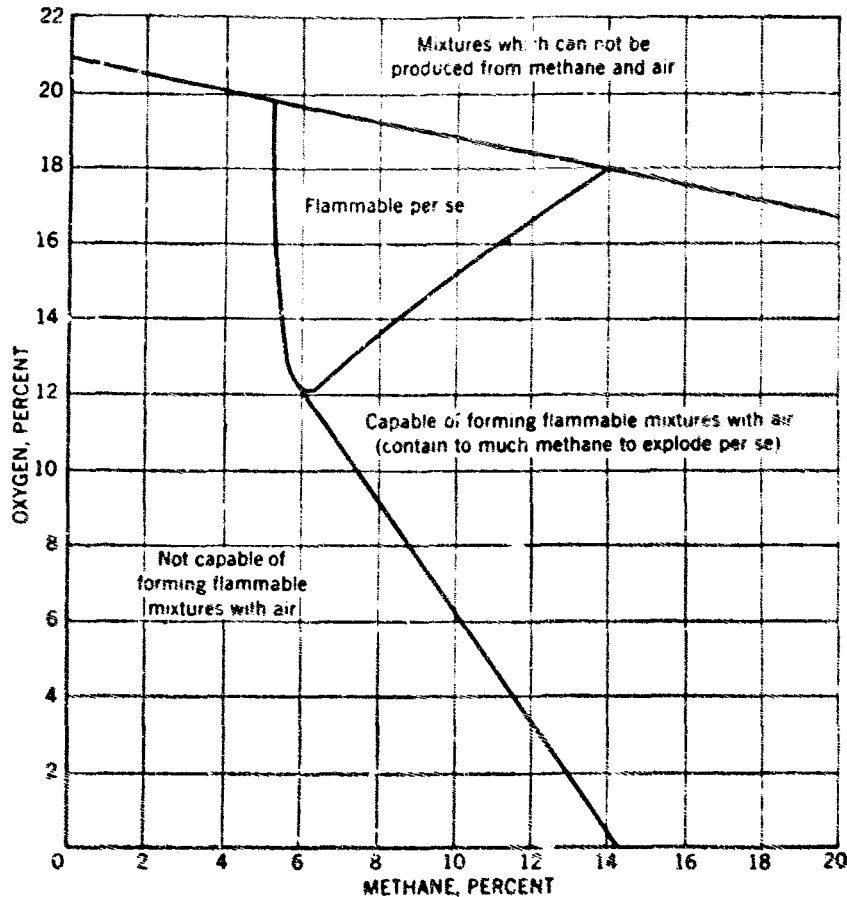
Figure 22.—Relation Between Quantitative Composition and Flammability of Mixtures of Methane, Air, and Nitrogen.

as its composition is represented by any point on *HJ*.

It will now be clear that the position of *FF* is exactly defined by drawing a tangent from *A* to the curve *BEC* and extending the tangent to meet the axis of abscissas in *F*, because the line joining any point above and to the right of *FE* to *A* must pass through *BEC*, while the line joining any point below and to the left of *FE* to *A* must fail to pass through the explosive region *BEC*. *FE* is therefore the boundary of those mixtures capable of forming explosive mixtures with air.

Figure 22 shows clearly that any mixture of methane and nitrogen that contains more than about 14.3 percent methane can form explosive mixtures with air. If oxygen is present a correspondingly smaller amount of methane suffices.

Mixtures of methane, nitrogen, and oxygen that are represented by any point in the area *DCEF* of figure 23 can form explosive mixtures when mixed with air in suitable proportions. If it is of interest to know what these propor-

tions are—and if there is a wide range of possible explosive mixtures the danger is so much the greater—then they can be found from the following considerations:

Suppose the mixture of methane, nitrogen, and oxygen is represented by the point *G* in the area *DCEF*, then the straight line *GA* represents all possible mixtures of the original mixture and air. As the original mixture is diluted step by step with air, the composition of the new mixture is represented by points farther and farther along *GA*. The air mixture first becomes explosive *per se* at the point *H*, where *GA* crosses *EC*. The higher limit of the original mixture is defined by this point; the lower limit of the original mixture is defined by the point *J*, at which the *GA* cuts *EB*.

The ratio *AH* : *HG* is the ratio of original mixture to air in the upper-limit mixture, and the ratio *AJ* : *JG* is the ratio for the lower-limit mixture. Hence the limits of flammability of the original mixture are given in percentages by 100 *AJ*/*JG* (lower limit) and 100 *AH*/*HG* (higher limit) *(62)*.
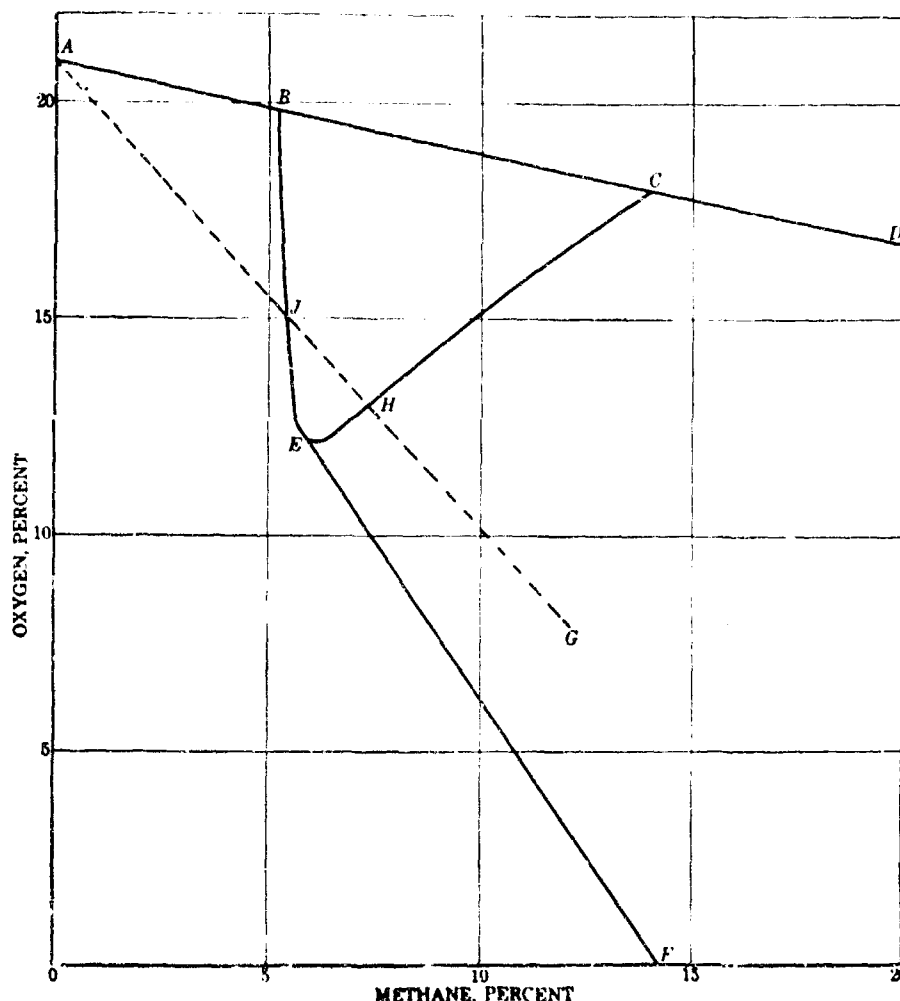
FIGURE 23. —Explanation of figure 22.

All Atmospheres of Oxygen and Nitrogen.— Limits of methane in these atmospheres have been determined with downward propagation of flame in a 1.7-cm.-diameter tube (345).

Atmospheres of Air and Water Vapor. Observations that show the small difference in the limits of methane in dry air and in air saturated with water vapor at laboratory temperatures are quoted under Effect of Small Changes in Atmospheric Composition (p. 3).

The effect of large amounts of water vapor on the limits of methane in air is shown in figure 24. The determinations were made in a tube 3 feet in length and 2 inches in diameter, with upward propagation of flame at atmospheric pressure during propagation (67). For each experiment the tube was heated to the temperature necessary to maintain the required amount of water vapor. Hence, most of the

observations were made at temperatures above normal. Had it been possible to experiment at normal temperature, the curve probably would have been a little to the right of the carbon dioxide curve over the lower-limit range and at the nose, but the two curves would have coincided over most of the higher-limit range.

Similar experiments have been made in a closed 350-cc. spherical vessel with a "natural gas" containing 97 percent methane, 3 percent ethane. Similar results were obtained, with somewhat smaller limits, which met at about 6.3 percent gas in a mixture containing about 30 percent of water vapor (568).

Atmospheres of Air and Carbon Dioxide.— Figure 25 shows the limits of methane in mixtures of air and carbon dioxide saturated with water vapor. The tests were made in a tube 7 feet in length and 10 inches in diameter, with
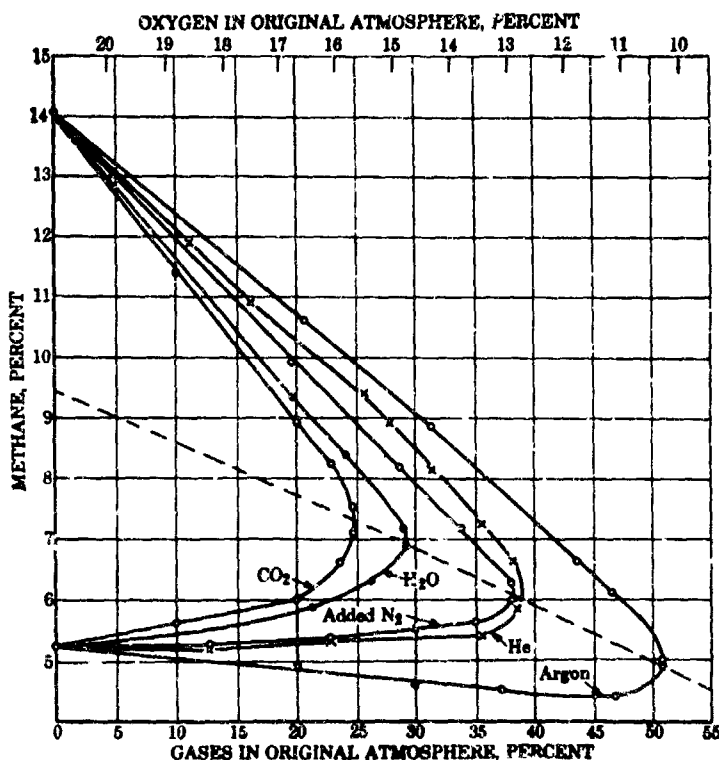
FIGURE 24.—Limits of Flammability of Methane in Separate Mixtures of Air with Carbon Dioxide, Water Vapor, Nitrogen, Helium, and Argon.

upward propagation of flame from the open end of the tube. In these circumstances no mixture of methane with an atmosphere composed of air and 24 percent or more carbon dioxide is capable of propagating flame far from the source of ignition (70)

Observations made in smaller apparatus are shown in figure 26. The results obtained in a 5-cm. tube with dry gases show, in general, a slightly wider range of flammability than those obtained in a 25-cm. tube with gases saturated with water vapor (fig. 25); for example, the completely extinctive atmosphere in the 5-cm. tube contains 25 percent carbon dioxide compared with 24 percent in the wider vessel. The four curves showing narrower limits represent experiments in various vessels with downward propagation of flame.

The limits of these mixtures with downward propagation of flame in a tube 2.2 cm. in diameter (341) and in a closed glass bulb 6.5 cm. in diameter (209) have also been determined.

Influence of Temperature.— The limits of firedamp in atmospheres of air and carbon dioxide have been determined from 100° to 600° C The firedamp used contained 73.8 percent methane and 26.2 percent nitrogen. The

observations were made in a horizontal glass tube 2 cm. in diameter and 100 cm. in length. The results are expressed in curves which show the limits of methane in the various atmospheres of air, carbon dioxide, and such additional nitrogen as was due to the firedamp itself. The curves are of the same type as those of figure 25 and show an increase in the range of flammability of all mixtures as the temperature is increased (10).

Atmospheres of Air, Nitrogen, and Carbon Dioxide (Including Mixtures of Air and Blackdamp).—The limits of methane in atmospheres of air, nitrogen, and carbon dioxide are plotted in figure 27; they were obtained with roughly dried gases in a tube 2 inches in diameter, with upward propagation of flame from the open end of the tube. The boundary at the right of the series of curves gives the limits in all atmospheres of ordinary air and carbon dioxide mixed in any proportions. The straight-line boundary at the left of the series of curves gives, with the oxygen figures inserted thereon, the limits in all atmospheres of air and nitrogen mixed in any proportions. The whole area between represents the limits in atmospheres which are deficient in oxygen and also contain carbon dioxide. When the deficiency of oxygen
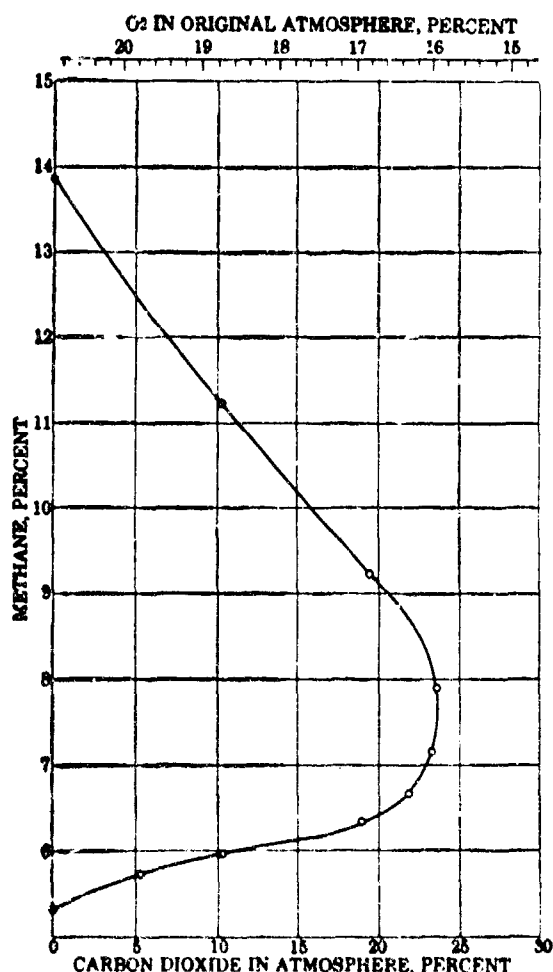
FIGURE 25. Limits of Flammability of Methane in Mixtures of Air and Carbon Dioxide (Experiments in Large Vessels).

is replaced by an equal amount of carbon dioxide, as would occur very nearly in the combustion of coke, these atmospheres and the corresponding methane limits are all represented by points on the broken curve.[7] The region right of the broken curve represents limits in atmospheres formed by the replacement of oxygen with more than an equal volume of carbon dioxide. The region left of the broken curve represents limits in atmospheres formed by the replacement of oxygen with less than an equal volume of carbon dioxide. Atmospheres of this type are produced by ordinary combustion, by respiration, and by mixing blackdamp and air (58).

As the composition of blackdamp is variable, its effect on the limits of methane is shown in figure 28 for a range of variations in composi-

[7] See reference 28 for earlier observations, made in a Bunte burette.

tion. These curves show that the lower limit of firedamp is increased only slightly by the presence of blackdamp and that the danger of an explosion of firedamp is not removed by the presence of blackdamp, unless the amount of blackdamp is so high that the atmosphere is not fit to work in even if gas masks are worn. An artificial supply of oxygen or air would be necessary for work in an atmosphere of blackdamp and air incapable of propagating an explosion of firedamp (58).

Figure 22 may be used to determine whether any given mixture of firedamp, blackdamp, and air is explosive or can explode if mixed with a suitable amount of air. The mixture is analyzed to determine the proportions of methane, oxygen, nitrogen, and carbon dioxide present. The carbon dioxide is assumed to be replaced by an equal volume of nitrogen, and the information required is read from the figure, as explained on page 46; in a coal mine the amount of carbon dioxide in such mixtures is about 5 or 6 percent (often less, rarely more), and the error introduced by considering this as nitrogen is small and on the side of safety (62).

Experiments with the same gases in small apparatus, with downward propagation of flame, have been reported, but on account of the experimental conditions the limits throughout are narrower and the extinctive amounts of inert gas are much less than those quoted above (309).

Atmospheres of Air and Argon or Helium.— Figure 24 shows the influence of nitrogen, water vapor, and carbon dioxide on the limits of flammability of methane in air, with upward propagation of flame in a tube 2 inches in diameter, with the firing end open. The different effects of the three gases are ascribed to their different heat capacities; as carbon dioxide has the greatest heat capacity, it has the greatest extinctive effect on flame. The corresponding curve for argon in the same figure agrees with this supposition, as argon has a smaller heat capacity than nitrogen. The curve for helium, a gas of heat capacity equal to argon, shows that this is not the only factor determining the extinctive effect of an inert gas; apparently the high thermal conductivity of helium makes it a more efficient flame extinguisher than argon. It seems, however, that the effect of different thermal conductivities is insignificant unless the difference is great (69).

The order of increasing efficacy of diluents, according to figure 24, is A, He, N_2, CO_2. Experiments with similar series of mixtures in narrow tubes (1.6 and 2.2 cm. in diameter), for downward propagation of flame, showed the same order of efficacy, except that the position of helium in the series varied with the diameter of the tube and, perhaps, with the strength of

FIGURE 26.— Limits of Flammability of Methane in Mixtures of Air and Carbon Dioxide; Comparison of Results Obtained in Smaller Vessels.

the igniting spark. (For a discussion of this important point, see p. 5.)

The broken line in figure 24 is the locus of mixtures in which the ratio of methane to oxygen is that required for complete combustion, $CH_4 : 2O_2$.

Atmospheres of Air and Sulfuryl Chloride, Silicon Tetrachloride, Silicochloroform, and Phosphorus Oxychloride.—The limits of methane in air with various amounts of sulfuryl chloride, silicon tetrachloride, silicochloroform, and phosphorus oxychloride have been determined in a burette 16 or 17 mm. in diameter (186, 195).

No mixture of methane and air containing more than 1.2 percent of phosphorus oxychloride was flammable in a 14.4-mm.-diameter tube, by a spark passed at the upper end of the tube, but mixtures containing up to 3.9 percent

could propagate flame upward in a 5-cm. tube (195).

Atmospheres of Air and Certain Halogenated Hydrocarbons.— Figure 29 shows the influence of certain chlorinated hydrocarbons, mixed in the stated amounts with air, on the limits of flammability of methane in a tube 2 inches in diameter with upward propagation of flame from the open end. Part of the carbon dioxide curve is inserted for comparison (71). The carbon tetrachloride curve has recently been redetermined independently, with nearly the same results (38).

The curves for trichloroethylene and tetrachloroethylene are incomplete; the experiments were carried to the point at which the atmosphere was saturated with these vapors at laboratory temperature. Tetrachloroethane and pentachloroethane, up to the saturation point,
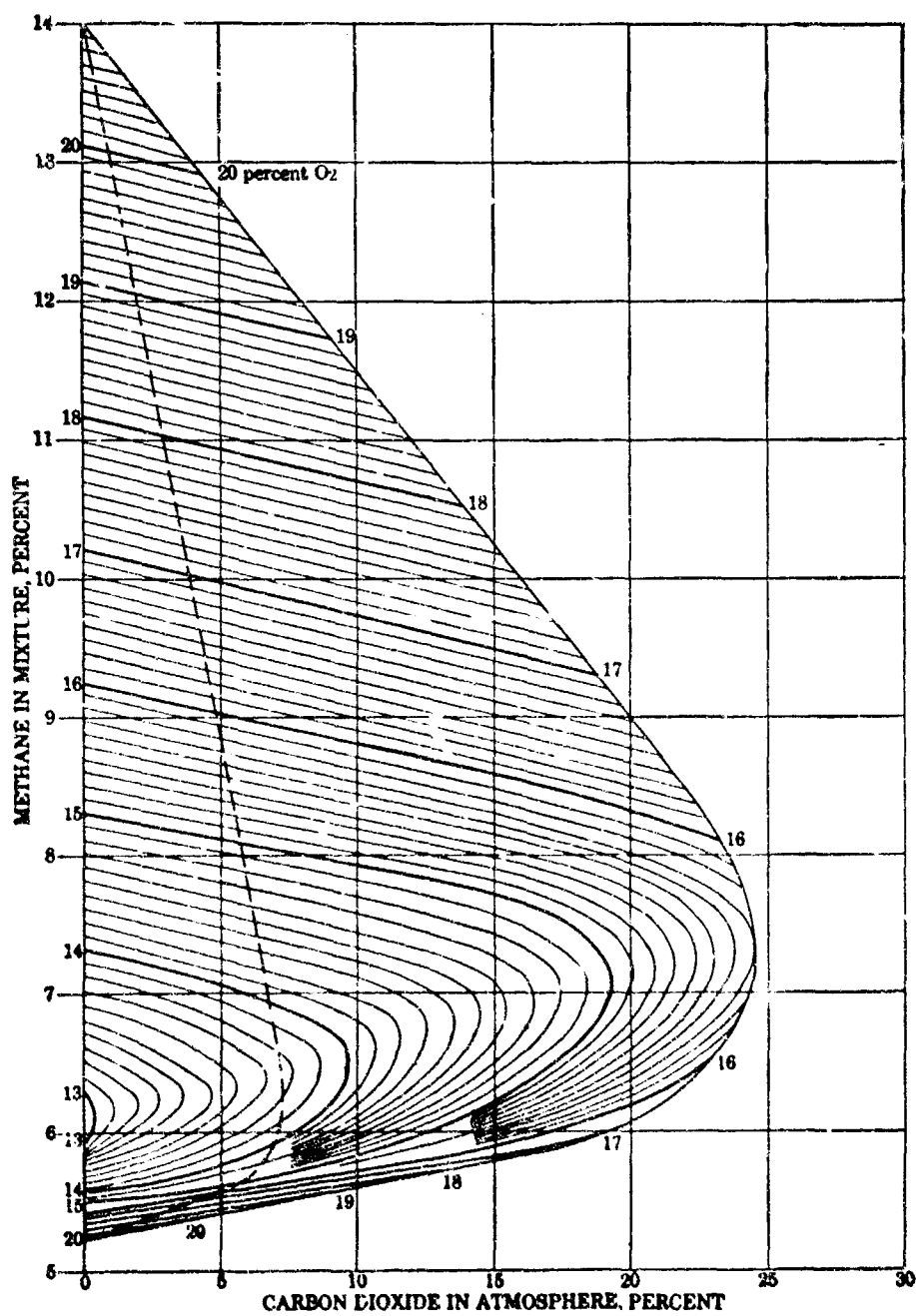
FIGURE 27.—Limits of Flammability of Methane in Mixtures of Air, Nitrogen, and Carbon Dioxide.
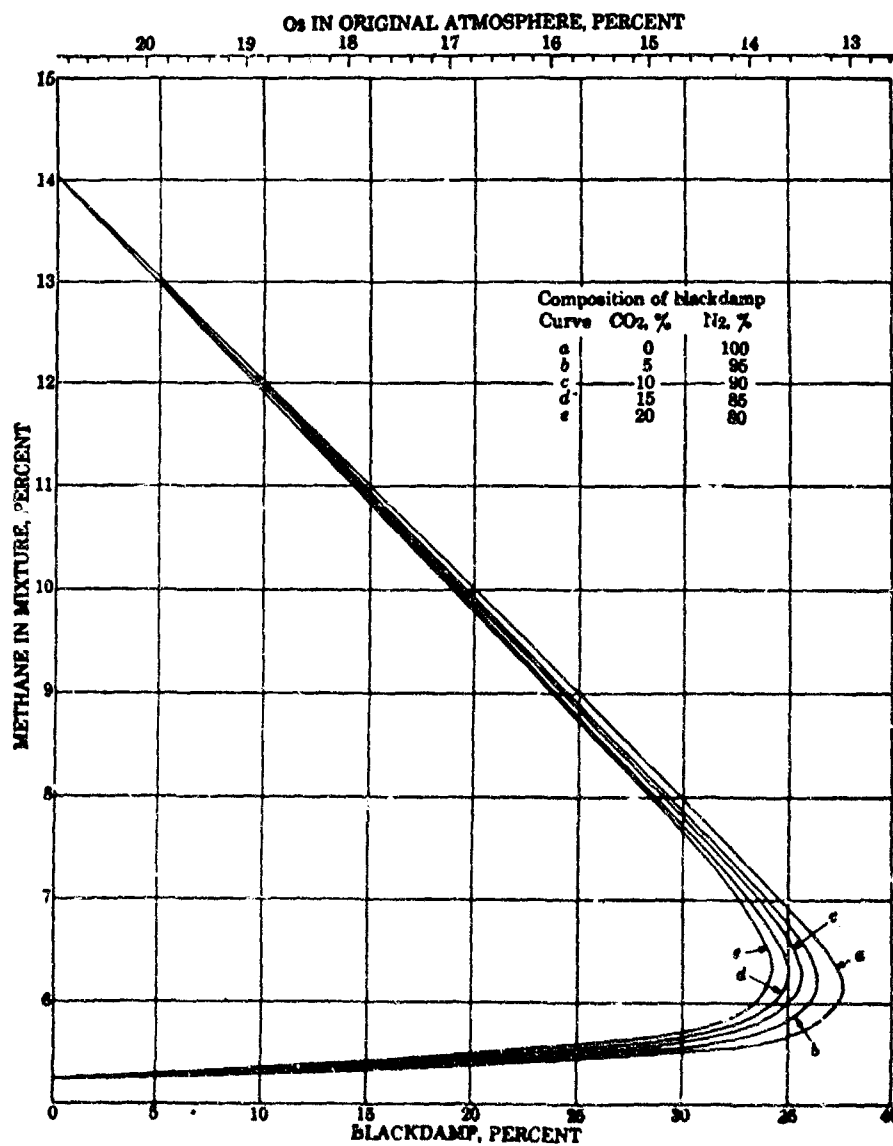
FIGURE 28.--Limits of Flammability of Methane in Mixtures of Air and Blackdamp.
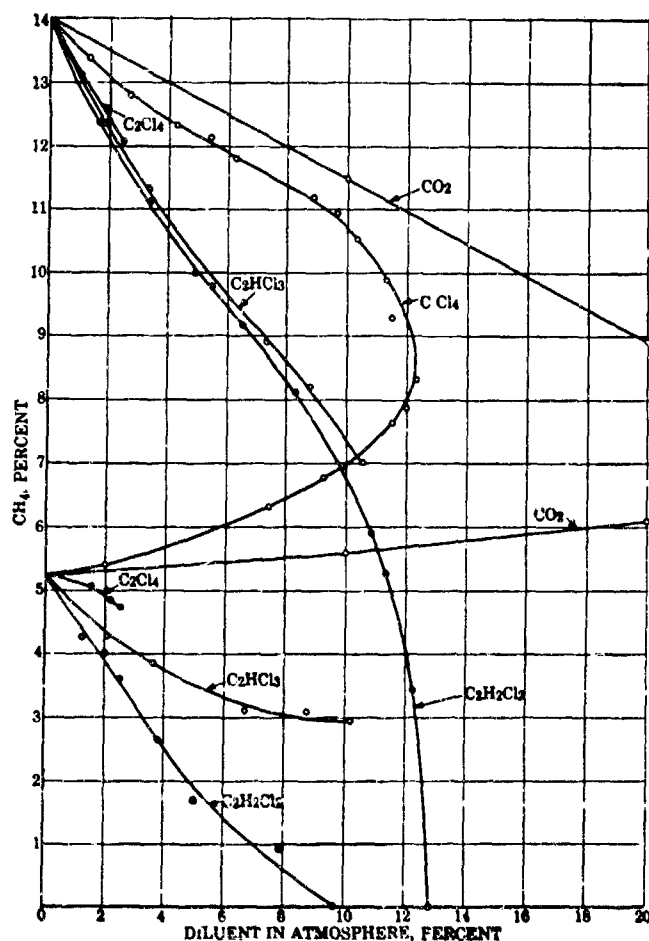
FIGURE 29.—Limits of Flammability of Methane in Mixtures of Air with Certain Chlorinated Hydrocarbons and with Carbon Dioxide.

behave like inert diluents whose effect is to be attributed to their thermal capacities. The ethylene derivatives, however, contribute to the flammability of the mixture, hence the lower limit of methane falls with an increase in the proportion of vapor; the higher limit also falls rapidly for the same reason. The order of increasing combustibility is $C_2Cl_4 \rightarrow C_2HCl_3 \rightarrow C_2H_2Cl_2$: the last vapor forms flammable mixtures with air without the help of any methane.

The extinctive effect of carbon tetrachloride on methane flames is due apparently entirely to its high thermal capacity. Volume for volume, carbon tetrachloride vapor is twice as extinctive as carbon dioxide, as the presence of 12.5 percent carbon tetrachloride in air renders the mixture incapable of propagating flame, whereas 25 percent carbon dioxide is necessary for the same effect. Equal volumes of the two liquids, however, have approximately equal extinctive effect.

The addition of increasing amounts of methyl bromide to the air causes the limits of methane to approach and, in a 2-inch-diameter tube, to meet at about 6 percent methane when 4.7 percent of the mixture is methyl bromide (38). For a comment, compare the corresponding paragraph on hydrogen (p. 22). An older series of experiments (260), made in almost identical circumstances, suggested higher results for both limits throughout the whole range of methyl bromide concentrations; these are partly explained by the criterion of "flammability" adopted for the older experiments, which was propagation of flame for at least 18 inches, not for the whole length of the tube.

The extinctive effect of dichlorodifluoromethane on methane flames (168) is almost exactly equal to that of carbon tetrachloride vapor, volume for volume.

Series of experiments with halogen derivatives, in narrow vessels with downward propagation of flame, have been reported (195, 197, 198, 199, 200) and discussed (71).

Atmospheres in Which the Nitrogen of the Air Is Replaced by Carbon Dioxide, Argon, or Helium.—The limits of methane in atmospheres in which the nitrogen of the air is replaced by (a) carbon dioxide, (b) argon, (c) helium, with upward propagation of flame in a 5.3-cm.-diameter tube open at the lower end, are (a) coincident at 9.0 percent, (b) 4.01 and 17.3 percent, and (c) 4.83 and 16.1 percent, respectively, in comparison with 5.26 and 14.3 percent in air. When the diameter of the tube is increased to 10 cm., the lower limit in the argon mixture is unaffected, but in the helium mixture it is reduced to 4.5 percent, showing that with helium mixtures in 5-cm. tubes the effect of the loss of heat to the walls is not negligible (94).

In a horizontal tube, 2.5 cm. in diameter, open at the firing end, the corresponding results are (a) 4.40 and 15.80 percent and (b) 5.55 and .25 percent (73).

In a closed globe of 35-cc. capacity, with side ignition, a corresponding result is (c) 8.9 and 11.7 percent methane (297).

Influence of Temperature.—In an atmosphere of 20.9 percent oxygen and 79.1 percent carbon dioxide, the limits in a closed 35-cc. globe were slightly widened by increase of temperature to 306° C. (297).

Atmospheres of Oxygen and Carbon Dioxide, and of Oxygen and Argon.—Limits of methane in these atmospheres have been determined with downward propagation of flame in a 1.7-cm.-diameter tube (345).

Atmospheres of Oxygen and Carbon Dioxide, Oxygen and Sulfur Dioxide, Nitrous Oxide and Carbon Dioxide, Nitrous Oxide and Sulfur Dioxide, and Oxygen and Nitrous Oxide.—Limits of methane in these atmospheres have been determined at pressures ranging from 600 mm. down to the point of coincidence of the limits (89).

Atmospheres of Nitrous Oxide and of Argon Mixed With Nitrous Oxide.—The limits of methane in nitrous oxide, with downward propagation of flame in a closed tube about 16 mm. in diameter, are 2.2 and 36.6 percent (206), 3.9 and 36.3 percent (339), and 4.1 and 41.2 percent at 600 mm. pressure (89). In a mixture of 2 volumes of nitrogen and 1 of oxygen, equivalent to nitrous oxide, the limits under similar conditions are 4.3 and 22.9 percent. The progressive addition of argon narrows the range, and no mixture with nitrous oxide is flammable under the conditions stated if it contains more than about 60 percent argon, or with the mixture of $2N_2+O_2$ if it contains more than about 67 percent argon (206).

Atmosphere of Nitric Oxide.—The limits of methane in nitric oxide, with downward propagation of flame in a closed tube 15 mm. in diameter, are 8.6 and 21.7 percent (339).

Atmospheres of Nitrous and Nitric Oxides.—The region of flammability of mixtures of methane with mixtures of nitrous and nitric oxides is plotted in a triangular diagram (339).

Influence of Small Amounts of "Promoters."—The addition of about 0.5 percent of various possible "promoters" (diethyl peroxide, ethyl nitrate, ozone, ether, ethyl alcohol) had little more effect on the limits of methane in air (upward propagation) than that due to the thermal effect of their reaction. With nitrogen peroxide, 0.5 percent reduced the lower limit by 0.33 percent (93) and 0.2 percent by 0.26 percent (70). The lower limit with downward propagation was not appreciably affected by up to 1.0 percent of nitrogen peroxide (70). With methyl iodide, 0.5 percent reduced the range from 5.26 to 14.3 percent to 6.29 to 12.3 percent (93).

Dilution of CH_4+2O_2 With Gases, Inert or Otherwise.—The following results were obtained with downward propagation of flame in a Bunte burette 1.9 cm. in diameter.

Effects of diluents upon flammability of $CH_4 + 2O_2$

Diluent:	Amount of CH_4+2O_2 which, with diluent named, is present at limit of flammability, percent
Oxygen	19. 3
Nitrogen	23. 3
Carbon dioxide	31. 9

Nitrogen has a greater extinctive action than oxygen, although it has less heat capacity; carbon dioxide, which has much greater heat capacity, also has a greater extinctive action (95).

With upward propagation of flame in a tube 5 cm. in diameter, the limits were found by the writers to be 11.85 percent CH_4+2O_2 when diluted with argon and 15.0 percent when diluted with helium. The effect of the difference in thermal conductivity is noteworthy.

ETHANE

ETHANE IN AIR

The limits of ethane in air, nearly dry, with upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, were found at various times to be 3.22 and 12.45 percent (74), 3.1 and 12.5 (146), and 2.90 and 12.50 percent (138).

Table 16 summarizes other determinations of the limits of ethane in air.

The higher limit varies more than the lower with the direction of propagation of flame. In closed tubes the higher limit is apparently much affected by the pressure developed during inflammation.

TABLE 16.— *Summary of other determinations of limits of ethane in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7. 5	150	Closed_____	3. 12	14. 95	Half-saturated_____	356
5. 0	150	____do_____	3. 15	14. 8	____do_____	356

Horizontal Propagation of Flame

7. 5	150	Closed_____	3. 15	12. 85	Half-saturated_____	356
5. 0	150	____do_____	3. 22	11. 75	____do_____	356
2. 5	150	Open_____	3. 3	10. 6	Saturated_____	271

Downward Propagation of Flame

7. 5	150	Closed_____	3. 26	10. 15	Half-saturated_____	356
5. 0	150	____do_____	3. 32	10. 6	____do_____	356
2. 0	40	____do_____	3. 13	9. 85	_____	277
1. 9	40	____do_____	4. 05	9. 55	Saturated_____	323

Propagation in Globes

Capacity:					
"Large"_____	Closed_____	3. 4	10. 7	_____	350
4,000 cc_____	____do__	3. 1			35
2,000 cc_____	____do__	3. 1		Dry	32
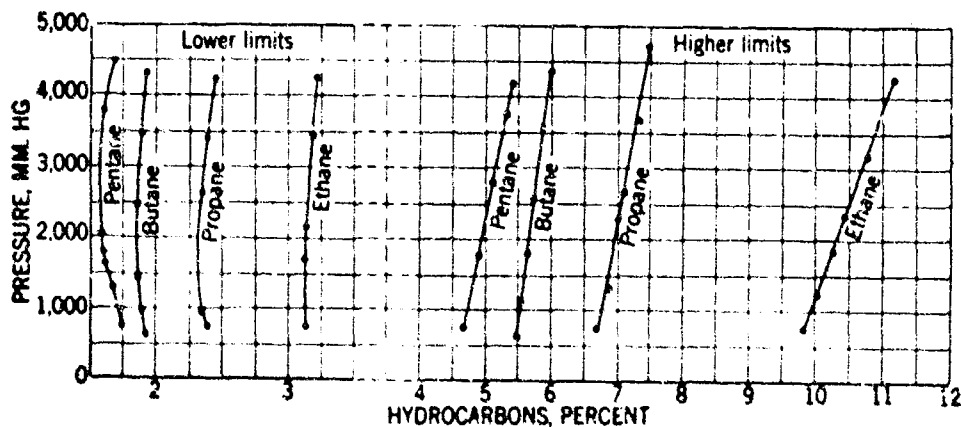
FIGURE 30.—Influence of Pressure on Limits of Some Paraffin Hydrocarbons (Downward Propagation of Flame

Influence of Turbulence.— In a 4-liter globe the lower limit for a quiescent mixture was 3.10 percent ethane; with a fan running at high speed inside the vessel a 3.2-percent mixture did not ignite; but when the fan was run at a moderate speed a 3.0-percent mixture exploded, producing a pressure of 4.3 atmospheres (350)

Influence of Pressure. Observations (277) in a closed tube 2 cm. in diameter and 40 cm.

in length, with downward propagation of flame are plotted in figure 30.   (For a discussion of these, see p. 3.)

ETHANE IN OXYGEN

The limits of ethane in oxygen with upward propagation of flame in a tube 2 cm. in diameter, open at the firing end, are 3.05 and 66.0 percent (144, 150).

An old observation placed the higher limit at 50.5 percent ethane with downward propagation of flame in a 2-cm. eudiometer (243).

ETHANE IN OTHER ATMOSPHERES

Atmospheres of Composition Between Air and Pure Oxygen.—The lower limit of ethane with downward propagation of flame in a Bunte burette 1.9 cm. in diameter was hardly altered as the oxygen in the atmosphere was increased to 94 percent; the higher limit rose gradually from 9.5 in air to 33.4 in a 60-percent oxygen mixture and to 46 in a 94-percent oxygen mixture (323).

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of ethane in all mixtures of air and nitrogen, or air from which part of the oxygen has been removed, are shown in figure 31. The determinations were made in a tube 2 inches in diameter and 6 feet in length, with upward propagation of flame at atmospheric pressure during propagation. From the ordinates of the "nose" of the curve it may be calculated that no mixture of ethane, nitrogen, and air can propagate flame at atmospheric pressure and temperature if it contains less than 11.0 percent oxygen (146).

Atmospheres of Air and Carbon Dioxide.— The limits of ethane in all mixtures of air and
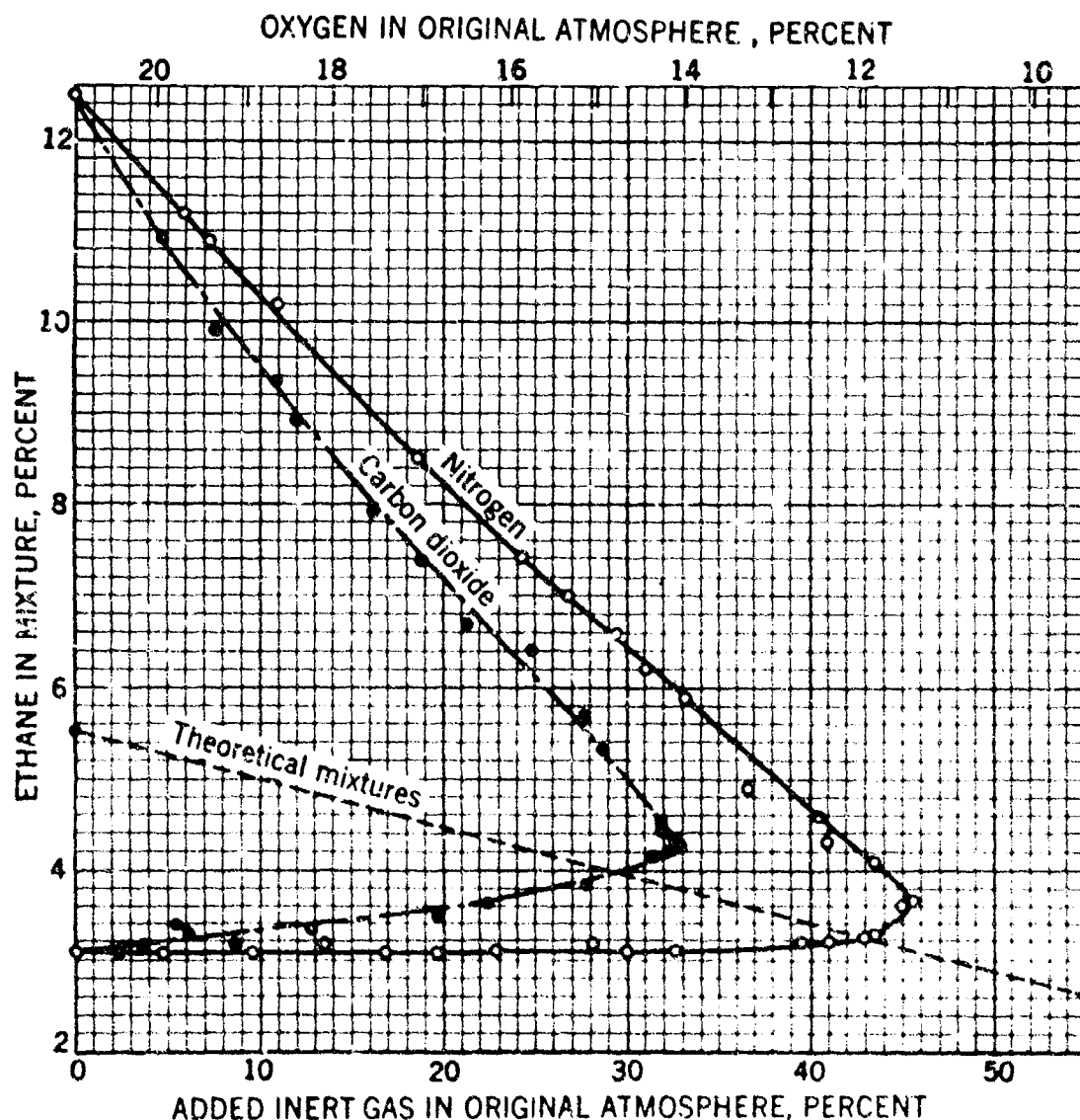
FIGURE 31.—Limits of Flammability of Ethane in Mixtures of Air and Nitrogen, and of Air and Carbon Dioxide.

carbon dioxide are shown in one of the curves in figure 31. The determinations were made as described in the previous paragraph (*146*).

PROPANE

PROPANE IN AIR

The limits of propane in air, nearly dry, with upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, are 2.37 and 9.50 percent (*74*), 2.15 and 9.05 percent (*179*).

The lower limit with a stationary horizontal flame (p. 10) in a mixture rising at a rate of about 5 cm. per sec., was, with a small correction for preheating, 2.12 percent of propane (*286*).

Table 17 gives other determinations of the limits of propane in air.

Influence of Pressure and Temperature.

The limits of propane in air, with horizontal propagation of flame in a bomb 3.8 cm. in diameter and 15.3 cm. in length at 100° C., are given in a diagram (*127*). The range of flammability widens from about 2 to 9 percent at atmospheric pressure to 2 to 17 percent at 12 atmospheres. "Cool" flames then make their appearance in rich mixtures and extend the higher limit to 23.4 percent at 19.3 atmospheres.

Observations (*277*) in a closed tube 2 cm. in diameter and 40 cm. in length, with downward propagation of flame at atmospheric temperature and pressures up to about 6 atmospheres, are plotted in figure 30. (For a discussion of these, *see* p. 3.)

TABLE 17.—*Summary of other determinations of limits of propane in air*

Horizontal Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
2.5	150	Open	2.4	7.3	Saturated	271

Downward Propagation of Flame

| 2.0 | 40 | Closed | 2.40 | 6.60 | | 277 |

Propagation of Globes

Capacity:						
"Large"		Closed	2.5	7.3		271
2,300 cc		do	2.17		Dry	52

On reducing the pressure below atmospheric, the limits approach and ultimately meet at about 100 mm. pressure (*157*, *125*).

PROPANE IN OXYGEN

The limits of propane in oxygen, with upward propagation of flame in a 2-inch-diameter tube open at its lower end, are 2.4 and 57 percent (*234*, 2.25 and 52.6 percent (*138*).

PROPANE IN OTHER ATMOSPHERES

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of propane in all mixtures of air and nitrogen can be read from

one of the curves in figure 32. The determinations were made in a tube 2 inches in diameter and 6 feet in length, with upward propagation of flame at atmospheric pressure during propagation. From the ordinates of the "nose" of this curve it may be calculated that no mixture of propane, nitrogen, and air at atmospheric pressure and temperature can propagate flame if it contains less than 11.6 percent oxygen (*147*).

Atmospheres of Air and Carbon Dioxide.—The limits of propane in all mixtures of air and carbon dioxide are shown in figure 32. The determinations were made as described in the previous paragraph (*147*).

Atmospheres of Air and Dichlorodifluoromethane.—The addition of dichlorodifluoromethane to air narrows the range of flammability of propane until, when 13.4 percent or more is present, no mixture is flammable (*170*).

Influence of Small Amounts of "Promoters."—The addition of about 0.5 percent of various possible "promoters" (diethyl peroxide, acetaldehyde, ether, ethyl alcohol) had little more effect on the limits of "propagas" (96
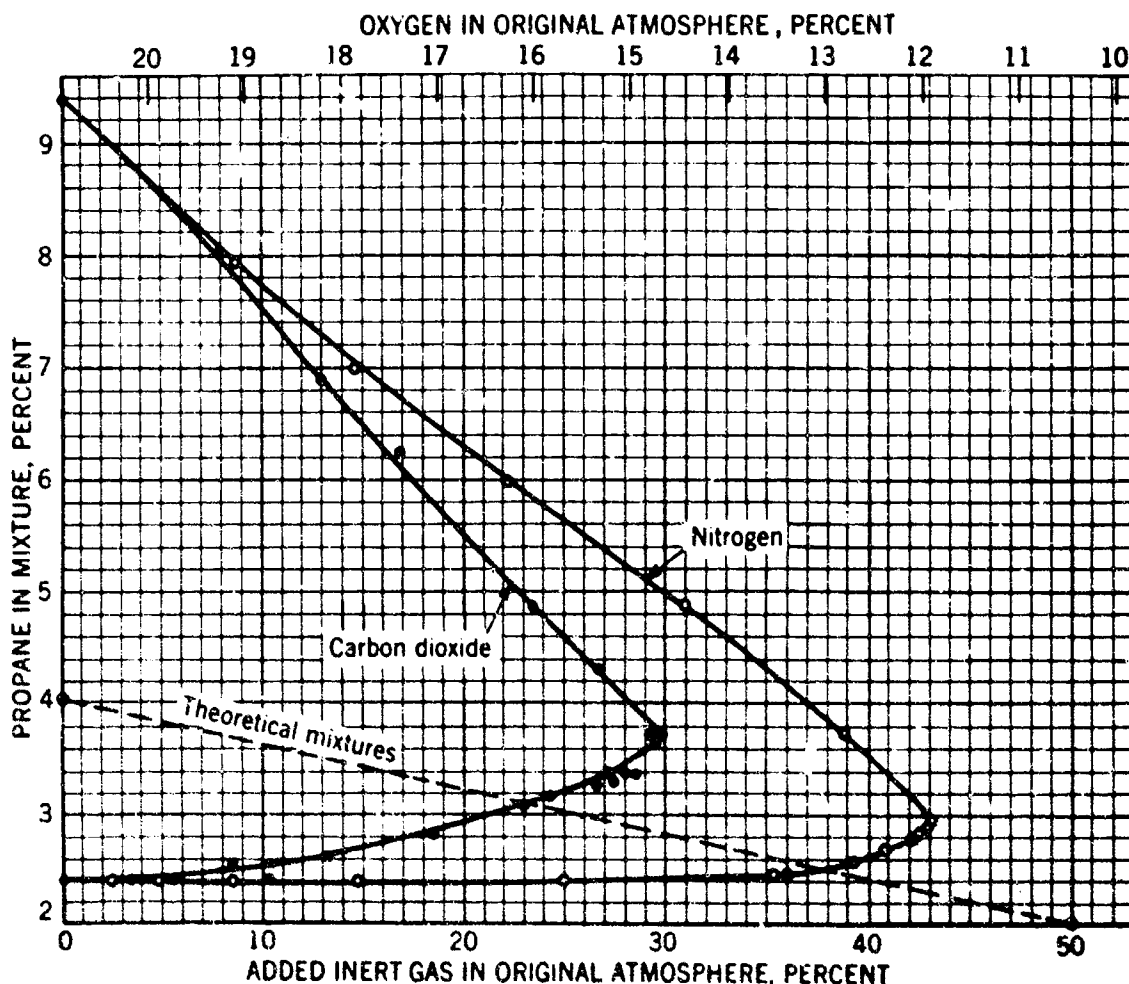
FIGURE 32.—Limits of Flammability of Propane in Mixtures of Air and Nitrogen, and of Air and Carbon Dioxide.

Atmospheres of Nitrogen Peroxide, and of Air and Nitrogen Peroxide (N$_2$O$_4$= 2NO$_2$).—The limits of propane in nitrogen peroxide and in mixtures of air and nitrogen peroxide (N$_2$O$_4$=2NO$_2$), with upward propagation of flame in a tube 4.3 cm. in diameter, open at the top, are shown in figure 33. The results are given on a weight basis, since the volume of peroxide is less easily ascertainable (*123*).

percent C$_3$ hydrocarbons, 4 percent C$_4$ hydrocarbons, 96 percent saturated) in air (upward propagation of flame) than that due to the thermal effect of their reaction. The same amount of nitrogen peroxide reduced the lower limit by 0.14 percent and increased the higher limit by 0.2 percent. Ethyl nitrate (0.5 percent) increased the higher limit from 9.6 to 12.4 percent (*93*).
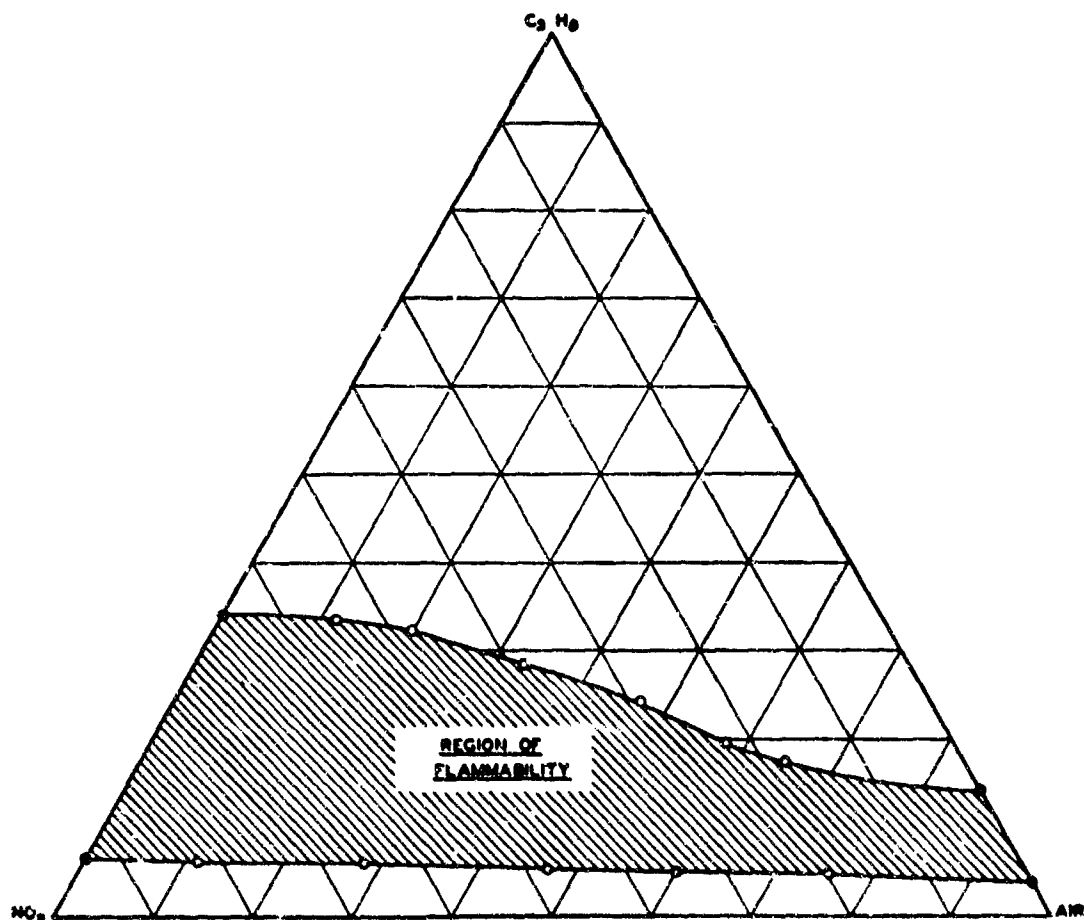
FIGURE 33.—Weight Percent Composition of Flammable Mixtures of Air, Nitrogen Peroxide, and Propane.

BUTANE

BUTANE IN AIR

The limits of butane in air, nearly dry, with upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, were 1.86 and 8.41 percent (74); 1.85 and 8.10 (170); and in a slightly wider tube (5.3 cm. diameter) 1.93 and 9.05 percent (93).

The lower limit with a stationary horizontal flame (p. 10), in a mixture rising at a rate of about 5 cm. per second, was, with a small correction for preheating, 1.69 percent of butane (286).

Table 18 gives other determinations of the limits of butane-air mixtures.

Influence of Pressure and Temperature.—The limits of butane in air, with horizontal propagation of flame in a bomb 3.8 cm. in diameter

and 15.3 cm. in length, at 100° C., are given in a diagram (127). The range of flammability widens from about 2 to 8 percent at atmospheric pressure, to 2 to 16 percent at 10 atmospheres. "Cool" flames then make their appearance in rich mixtures and extend the higher limit to 26 percent at 15.5 atmospheres.

Observations (277) in a closed tube 2 cm. in diameter and 40 cm. in length, with downward propagation of flame at atmospheric temperature and pressure up to about 6 atmospheres, are plotted in figure 30. (For a discussion of these, see p. 3.)

BUTANE IN OXYGEN

The limits of butane in oxygen with upward propagation of flame in a tube 2 inches in diameter, open at the firing end, are 1.85 and 49.0 percent (138).

BUTANE IN OTHER ATMOSPHERES

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of butane in all mixtures of air and nitrogen are shown in figure 34. The determinations were made in a tube 2 inches in diameter and 6 feet in length, with upward propagation of flame at atmospheric pressure during propagation. From the ordinates of the "nose" of the curve it may be calculated that no mixture of butane, nitrogen, and air at atmospheric pressure and temperature can propagate flame if it contains less than 12.1 percent oxygen (147).

Atmospheres of Air and Carbon Dioxide.—The limits of butane in all mixtures of air and carbon dioxide are shown in figure 34. The determinations were made as described in the previous paragraph (147).

Atmospheres of Air and Argon or Helium.—The limits of butane in mixtures of air with argon and with helium, with downward propagation of flame in a tube 2.2 cm. in diameter, have been determined (341).

Atmospheres of Air and Dichlorodifluoromethane.—The addition of dichlorodifluoromethane to air narrows the range of flamma-

TABLE 18.—*Summary of other determinations of limits of butane in air*

Horizontal Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
2.5	150	Open	1.9	6.5	Saturated	2

Downward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
2.2		Closed	2.2	7.4		341
2.0	40	do	1.92	5.50		277

Propagation in Globes

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
Capacity: "Large"		Closed	1.6	5.7		271
2,000 cc.		do	1.65		Dry	32

bility of butane until, when 13.2 percent or more is present, no mixture is flammable (170). In a 1.6-cm. tube with downward propagation of flame the corresponding figure is 8 percent (340).

Atmospheres of Nitrous and Nitric Oxides.—The limits of butane in nitrous oxide, with downward propagation of flame in a tube 18 mm. in diameter, are approximately 2.5 and 20 percent. In nitric oxide, with downward propagation in a 15-mm. burette, the limits are 7.5 and 12.5 percent (339).

Influence of Small Amounts of "Promoters."—The addition of 0.5 percent of various possible "promoters" (diethyl peroxide, ethyl nitrate, nitrogen peroxide, nitromethane, ether, acetaldehyde, methyl iodide, ethyl borate) had little more effect on the lower limit of butane in air (upward propagation) than that due to the thermal effect of their reaction. Some of the "promoters," especially ethyl nitrate, affected the higher limit, apparently by some catalytic action. A trace of lead tetraethyl narrowed the range of flammability slightly (93).
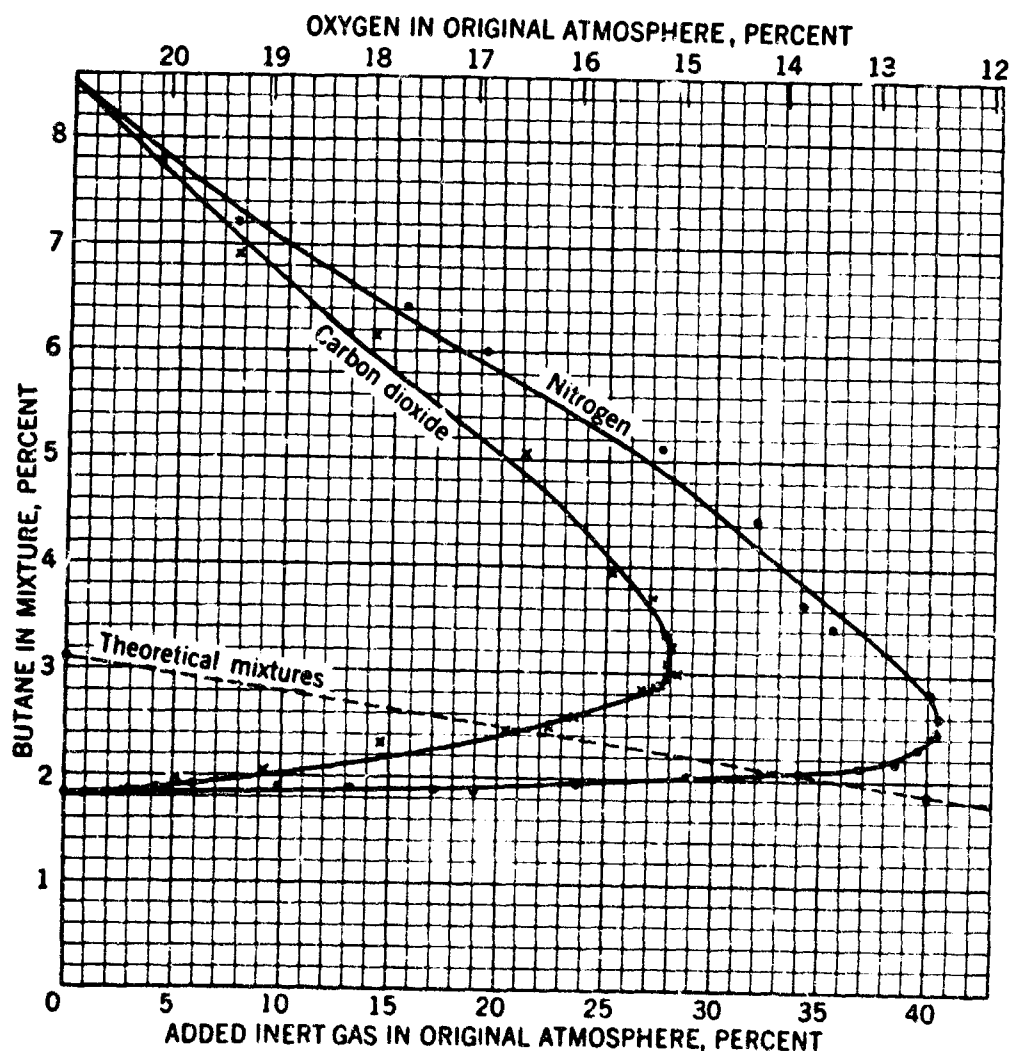
FIGURE 34.—Limits of Flammability of Butane in Mixtures of Air and Nitrogen, and of Air and Carbon Dioxide.

ISOBUTANE

ISOBUTANE IN AIR

The limits of isobutane in air with upward propagation of flame in a tube 2 inches in diameter and 6 feet in length at approximately atmospheric pressure are 1.83 and 8.43 percent (175).

ISOBUTANE IN OXYGEN

The limits of isobutane in oxygen with upward propagation of flame in a tube 2 inches in diameter, open at the firing end, are 1.80 and 48.0 percent.

ISOBUTANE IN OTHER ATMOSPHERES

Atmospheres of Air and Nitrogen, and of Air and Carbon Dioxide.—The limits of iso-

butane in atmospheres of air and nitrogen, and of air and carbon dioxide, are almost identical with the corresponding limits of butane (175).

PENTANE

PENTANE IN AIR

The limits of pentane in air, with upward propagation of flame in a tube 5 cm. in diameter and open at the firing end, are 1.42 and 7.80 [a] percent (135) and in a similar tube 5.3 cm. in diameter the lower limit is 1.62 percent (94).

[a] The pentane used in the determination of these limits was supplied by the American Petroleum Institute, Research Project 45, C. E. Boord, Director. Limits reported for n-hexane, cyclohexane, ethyl cyclobutane, ethyl cyclopentane, n-heptane, methyl benzene (toluene), ethyl cyclohexane, 3,3 diethyl pentane, 2,2,3,3 tetramethyl pentane, diethyl benzene, n-butyl benzene, sec. butyl benzene, isobutyl benzene, and tert-butyl benzene, by Bureau of Mines (ref. 135) in various sections of this bulletin, were obtained with samples of high purity supplied by the above institute.

TABLE 19.—*Summary of other determinations of limits of pentane in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed_____	1.42	8.0	Half-saturated_____	*356*
5.0	150	_____do_____	1.43	8.0	_____do_____	*356*

Horizontal Propagation of Flame

7.5	150	Closed_____	1.44	7.45	Half-saturated _____	*356*
5.0	150	__do_____	1.46	6.70	_____do_____	*356*
2.5	150	Open_____	1.6	5.4	Saturated_____	*271*

Downward Propagation of Flame

7.5	150	Closed _____	1.48	4.64	Half-saturated_____	*356*
6.2	33	Open _____	1.3	_____	Saturated_____	*95*
5.0	150	Closed_____	1.49	4.56	Half-saturated_____	*356*
5.0	65	____do_____	1.43	4.6	Dry_____	*316*
5.0	65	Open _____	1.50	4.75	_____	*23*
2.0	40	Closed _____	1.75	4.68	_____	*277*
1.9	40	_____do_____	2.4	4.9	Saturated_____	*95*

Propagation in Vessels Other Than Tubes

Capacity:					
Globe, 14.5 liters	_____	1.2	_____	_____	*95*
Large	_____	1.4	4.5	_____	*271*
Bottle, 2 liters	Open_____	1.1	_____	_____	*220*
Globe, 2 liters	_____	1.37	_____	_____	*32*

Tables 19 summarizes other determinations of the limits of pentane in air.

Influence of Pressure.—Observations (*277*) in a closed tube 2 cm. in diameter and 40 cm. in length, with downward propagation of flame, are plotted in figure 30. (For a discussion of these curves, *see* p. 3.)

The effect of reduced pressure on the limits of ignitibility of pentane by a standard spark, rather than its limits of flammability, have been reported (*13*).

Influence of Temperature.—In a closed tube 2.5 cm. in diameter and 150 cm. in length, with downward propagation of flame, the lower limit decreased linearly from 1.53 percent at about 17° C. to 1.22 percent at 300° C.; the higher limit increased linearly from 4.50 percent at about 17° C. to 5.35 percent at 300° C. (*356*).

PENTANE IN OTHER ATMOSPHERES

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of pentane in all mixtures of air and nitrogen are shown in figure 35. The determinations were made in a tube 2 inches in diameter and 6 feet in length, with upward propagation of flame at atmospheric pressure during propagation. From the ordinates of the "nose" of the curve it may be calculated that no mixture of pentane, nitrogen, and air at atmospheric pressure and temperature can propagate flame if it contains less than 12.1 percent of oxygen (*138*).

Atmospheres of Air and Carbon Dioxide.—The limits of pentane in all mixtures of air and carbon dioxide are shown in figure 35. The determinations were made as described in the previous paragraph (*138*).
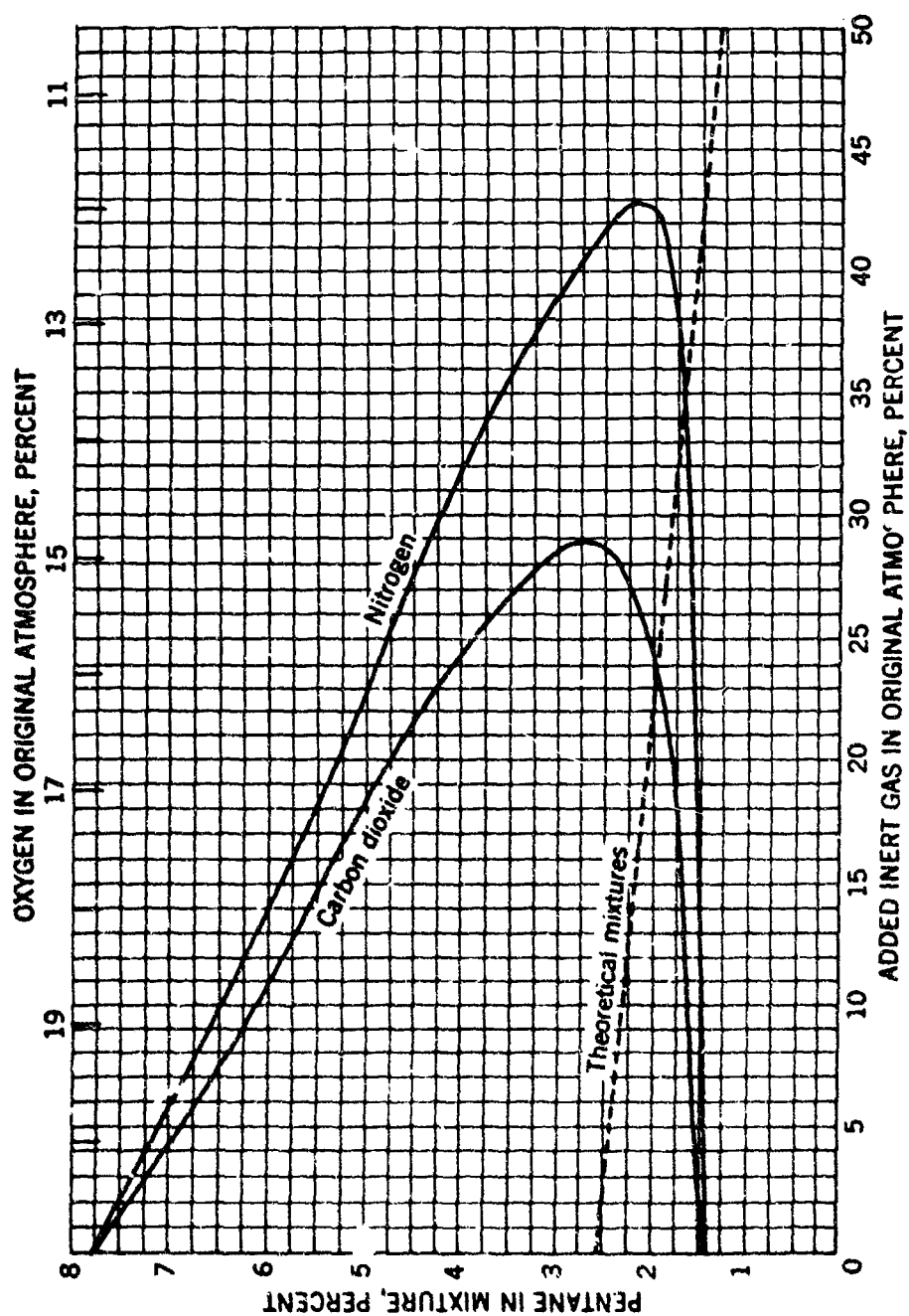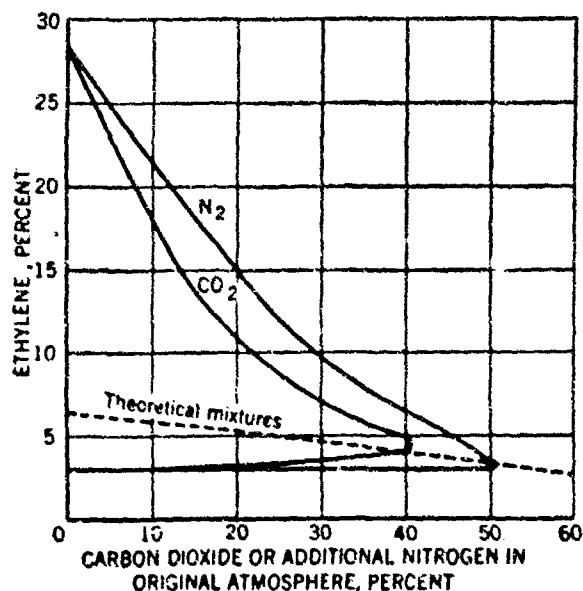
FIGURE 35.—Limits of Flammability of Pentane in Mixtures of Air and Nitrogen, and of Air and Carbon Dioxide.

ISOPENTANE

The limits of isopentane in air, with upward propagation of flame in a 2-inch-diameter tube open at the lower end, the mixture being at 450 to 500 mm. pressure initially but attaining atmospheric pressure during the propagation of the flame, are 1.35 and 7.60 percent *(138)*.

The lower limit of isopentane in a 2-liter globe is 1.32 percent *(32)*.

Influence of Temperature.—The limits of isopentane in air with downward propagation of flame in a 2½-liter bottle widen from 1.43 and 4.85 percent at 100° C. to 1.10 and 5.25 at 250° C. *(21, 23)*.

2,2 DIMETHYLPROPANE

The limits of 2,2 dimethylpropane in air, with upward propagation of flame in a 2-inch-diameter tube open at the lower end, are 1.38 and 7.50 percent *(138)*.

HEXANE

HEXANE IN AIR

The limits of hexane in air in a 5-cm.-diameter tube are 1.27 and 6.90 percent *(149, 150)*, 1.18 and 7.43 percent *(138)*; in a 5.3-cm.-diameter tube the lower limit is 1.46 percent *(94)*; in a 4.8-cm.-diameter tube the limits are 1.45 and 7.50 percent; and in a 10.2-cm.-diameter tube 1.45 and 5.70 percent *(38)*, all with upward propagation of flame from an open end.

The lower limit of hexane in a 2-liter open bottle, apparently with downward propagation of flame, is 1.3 percent *(221)*; in a 6-cm. tube, with downward propagation of flame, the limits were about 1.2 and 3.6 percent *(325)*.

Influence of Impurities.—The limits of hexane in air were slightly narrowed by the presence of iron carbonyl (0.03 cc. of liquid vaporized per liter) *(325)*.

Influence of Pressure and Temperature.—The limits of hexane in air, with horizontal propagation of flame in a bomb 3.8 cm. in diameter and 15.3 cm. in length, at several temperatures and pressures up to 14 atmospheres, are shown in figure 36 *(127, 332)*. Normal flames were obtained up to 4 atmospheres, but at 4.1 atmospheres and 150° C. a "cool flame" appeared with mixtures from 11 to 22 percent of hexane, the normal flame being limited to mixtures from 1.2 to 7.0 percent. At pressures above 4.8 atmospheres the two ranges met; for example, at 6.5 atmospheres mixtures of 1 to 14.5 percent of hexane propagated normal flames and 14.5 to 32 percent propagated "cool" flames. Flames in mixtures up to 6.5 percent were whitish or yellowish, 6.5 to 11 percent

PRESSURE, ATMOSPHERES

HEXANE IN AIR, PERCENT
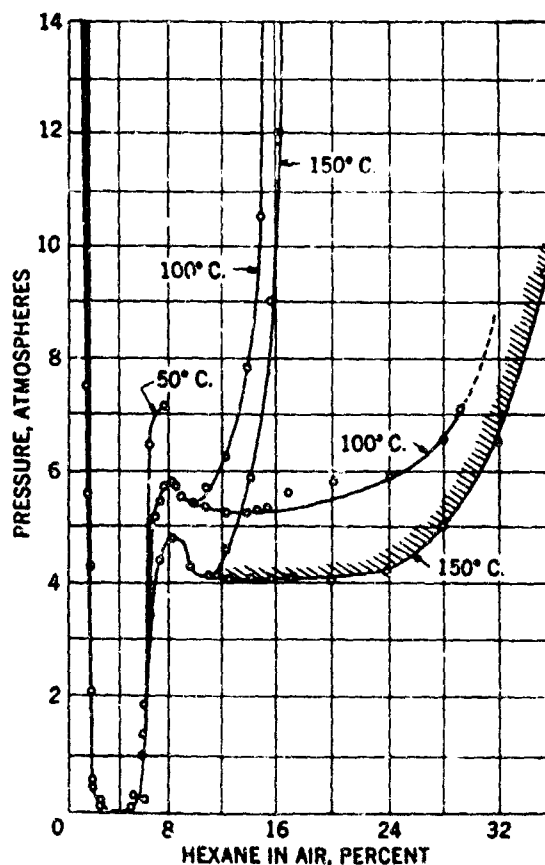
FIGURE 36.—Influence of Pressure on Flammable Ranges of Hexane-Air Mixtures.

orange or reddish (with deposition of carbon or tar), and beyond 11 percent blue (without carbon deposition, but with formation of much aldehyde).

The lower limit with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39 cm. in length, vented at its upper end, is 1.08 percent at room temperature, 0.90 percent at 100° C., and 0.72 percent at 200° C. *(239)*.

The limits of hexane in air have been determined in a 709-cc. bomb at temperatures up to 220° C. and pressures up to 11.7 atmospheres, but in this series the mixture was maintained at the experimental temperature and pressure for 30 to 45 minutes before testing, in order to allow preflame combustion to occur. The limits found are therefore of a complex mixture of unknown composition *(245)*.

Curves showing the influence of pressure up to 500 atmospheres on the limits of *n*-hexane in air have been given *(11)*, but the range of flammability seems to be impossibly wide.

The limits with horizontal propagation of flame in a 4.5-cm.-diameter tube, at 20° and

100° C. and pressures below atmospheric, are given in a diagram (*125*). The effect of reduced pressure on the limits of ignitibility of these mixtures by a standard spark, rather than their limits of flammability, have been examined (*13*).

HEXANE IN OXYGEN

The limits of hexane in oxygen, with horizontal propagation of flame in a bomb 3.8 cm. in diameter and 15.3 cm. in length, at 100° and 150° C. and 0 to 3 atmospheres pressure.

figure 38. The determinations were made in a tube 2 inches in diameter and 6 feet in length, with upward propagation of flame at atmospheric pressure during propagation. From the ordinates of the "nose" of the curve it may be calculated that no mixture of hexane, nitrogen, and air at atmospheric temperature and pressure can propagate flame if it contains less than 11.9 percent oxygen (*149*).

Atmospheres of Air and Carbon Dioxide.— The limits of hexane in all mixtures of air and
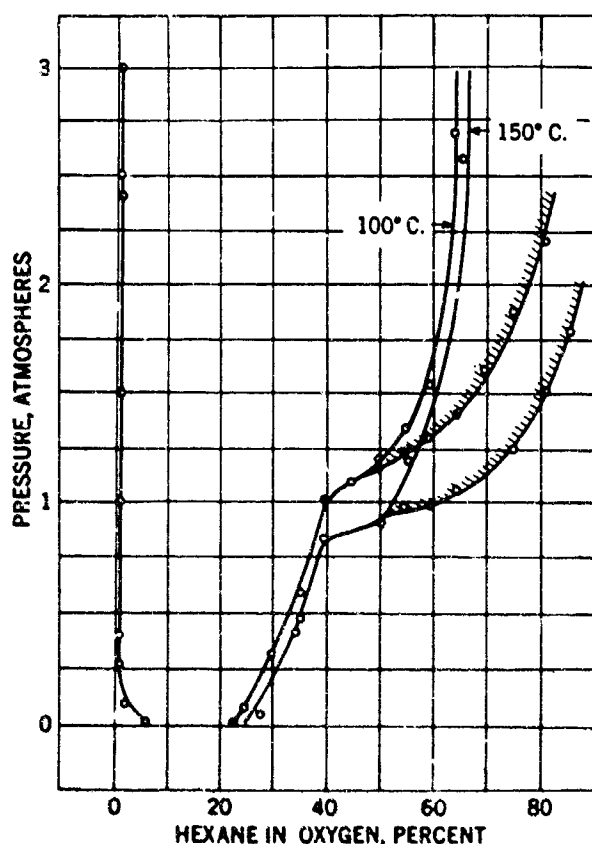
FIGURE 37.—Influence of Pressure on Flammable Ranges of Hexane-Oxygen Mixtures.

are shown in figure 37 (*127, 332*). "Cool"-flame ranges are indicated by the shaded branch curves. It will be seen that, at 150° C., cool flames can be obtained in certain hexane-oxygen mixtures at pressures from 0.9 atmosphere upward; the corresponding figure for hexane-air mixtures at 150° C. is 4.1 atmospheres.

HEXANE IN OTHER ATMOSPHERES

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen). —The limits of hexane in all mixtures of air and nitrogen are shown in

carbon dioxide are shown in figure 38. The determinations were made as described in the previous paragraph (*149*).

Atmospheres of Air and Certain Halogenated Hydrocarbons.—The addition of increasing amounts of methyl bromide to the air causes the limits of hexane to approach and, in a 2-inch tube, to meet when 7.05 percent of the mixture is methyl bromide; in a 4-inch tube, when 6.0 percent is methyl bromide. With dichlorodifluoromethane ("freon-12") in similar experiments, in a 2-inch-diameter tube, the corresponding figure is 13.5 percent of freon (*38*).
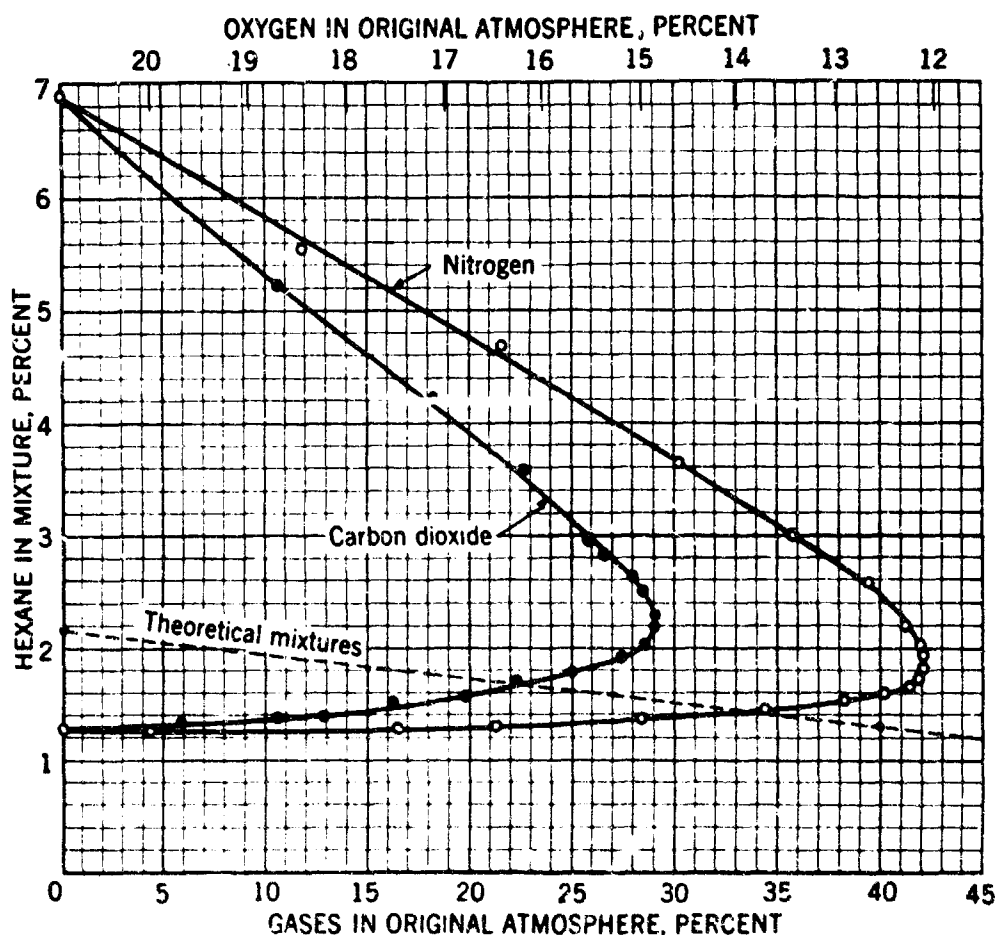
FIGURE 38.—Limits of Flammability of Hexane in Mixtures of Air and Nitrogen, and of Air and Carbon Dioxide.

DIMETHYL BUTANES

The limits of 2,2 and 2,3 dimethyl butanes in air, with upward propagation of flame in a 2-inch-diameter tube open at the lower end, are the same, 1.20 and 7.00 percent (138).

METHYL PENTANE

The limits of 2-methyl pentane in air, with upward propagation of flame in a 2-inch-diameter tube, 4 feet in length, closed at the lower end for the lower limit and open for the higher limit, are 1.18 and 6.95 percent (138).

HEPTANE

The limits of heptane in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 1.10 and 6.70 percent (138), and in a similar tube 5.3 cm. in diameter the lower limit is 1.26 percent (94).

The limits of heptane in air (dimensions of vessel and direction of flame propagation not stated) are 1 and 6 percent (101). An observation made in a 2-liter open bottle, apparently with downward propagation of flame, gave 1.1 percent as the lower limit of heptane in air (221).

DIMETHYL PENTANE

The limits of 2,3 dimethyl pentane in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 1.12 and 6.75 percent (138).

OCTANE

The lower limit of octane in air, with upward propagation of flame in a tube 2 inches in diameter, open at the firing end, is 0.95 percent (139), 1.00 percent (138), and in a similar tube 5.3 cm. in diameter, 1.12 percent (94). The lower limit in a 2-liter open bottle, apparently with downward propagation of flame, is 1.0 percent (221).

ISO-OCTANE

The lower limit of "iso-octane" (2,2,4 trimethyl pentane) in air, with upward propagation of flame in a tube 5.3 cm. in diameter, is 1.15 percent (94). In a tube 2.5 cm. in diameter, 18 inches in length, open at the top, the limits are 0.98 and 6.03 percent (138).

NONANE

The lower limit of nonane in air in a 2-liter open bottle, apparently with downward propagation of flame, is 0.83 percent (221).

DIETHYL PENTANE

The limits of 3,3 diethyl pentane in air, with upward propagation of flame in a 1-inch-diameter tube, open at its upper end and at a sufficient temperature to volatilize the diethyl pentane, are 0.74 and 5.75 percent (138).

TETRAMETHYL PENTANE

The limits of 2,2,3,3 tetramethyl pentane in air, with upward propagation of flame in a 2-inch-diameter tube, 18 inches in length, open at its upper end and at 100° C., are 0.77 and 4.90 percent (138).

DECANE

The lower limit of decane in air (dimensions of apparatus and direction of flame propagation not stated) is 0.67 percent (253).

More recent determinations of the limits of n-decane in air, with upward propagation of flame in a 2-inch-diameter tube, 18 inches in length, open at its upper end and at 100° C., are 0.77 and 5.35 percent (138).

DODECANE

The lower limit of dodecane in air (dimensions of apparatus, direction of flame propagation, and temperature not stated) is 0.60 percent (101).

PARAFFIN HYDROCARBONS IN GENERAL

PARAFFIN HYDROCARBONS IN AIR

The lower limits in air of members of the paraffin series, with upward propagation of flame in a 2-inch tube, are given approximately by the broken curve in figure 58 (as described on p. 114).

HIGHER-PARAFFIN HYDROCARBONS IN OTHER ATMOSPHERES

Atmospheres of Air and Carbon Tetrachloride.—Table 20 shows the minimum percentages, by volume, of liquid carbon tetra-

chloride that will render mixtures with various hydrocarbons nonflammable: (a) When the mixture is volatilized as completely as possible at room temperatures, (b) when a flame is presented momentarily to the free surface of the liquid mixture, and (c) when a flame is presented momentarily to the exposed end of a wick dipping into the mixture (148).

TABLE 20.—*Minimum percentages, by volume, of carbon tetrachloride in nonflammable mixtures with hydrocarbons*

Hydrocarbon	Vaporized (a)	Free liquid surface (b)	Liquid on wick (c)
Pentane	67	50	70
Hexane	70	63.5	67
Heptane	70	50	58
Octane	67	50	67
Naphtha	70	50	58
Gasoline	58	50	58

The amount of carbon tetrachloride that must be added to naphthas to render them "reasonably safe from fire hazards" is as follows (6):

Naphtha	Density	Distillation range, °C.	Carbon tetrachloride by volume required to render naphtha "reasonably safe from fire hazards," percent
1	0.758	120 to above 180	30
2	.725	80 to above 140	45
3	.698	50 to above 115	50
4	.681	50 to above 110	70

ETHYLENE

ETHYLENE IN AIR

The limits of ethylene in air, with upward propagation of visible flame in a tube 5 cm. in diameter, open at the firing end, are 3.05 and 28.6 percent (144), and 3.15 and 28 to 29 percent (38). An invisible flame, detectable by a resistance thermometer or thermocouple at the top of the tube, travels throughout the 150-cm. length of the tube in mixtures over the higher limit of visible flame propagation, up to 32.0 percent. When the diameter of the tube is increased to 10.2 cm. however, the limits are 3.20 and 22.7 percent only (38).

Table 21 summarizes other determinations of the limits of ethylene in air.

The higher limit depends very much on the direction of propagation of flame.

Influence of Pressure.— Experiments in a small cylindrical bomb (14) showed that pressure had a pronounced effect on the limits of

ethylene in air. The lower limit rose from 3.5 percent at normal pressure to 5 percent at 20 atmospheres, then fell to 1.5 percent at 380 atmospheres. The higher limit rose rapidly from 16 percent at normal pressure to 68 percent at 90 atmospheres, then rose slowly to 71 percent at 380 atmospheres.

At pressures below atmospheric, in a 1-inch-diameter tube, open at the firing end into a large reservoir of air which maintains almost constant pressure during the experiment, the limits converge and meet at about 90 mm. pressure. The higher-limit side of the curve shows irregularities in that, in certain ranges of pressure, there is a narrow range of composition in which flame is not propagated (104).

TABLE 21.—*Summary of other determinations of limits of ethylene in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
10. 2	96	Closed	2. 75	24. 0	Small	183
7. 5	150	do	3. 02	34	Half-saturated	356
6. 2	33	Open	3. 4	20. 55	do	95
5. 0	150	Closed	3. 13	33. 3	do	356
2. 5	150	do	3. 15	27. 6	do	356
2. 5	150	Open	3. 3	25. 6	Small	49

Horizontal Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7. 5	150	Closed	3. 29	23. 7	Half-saturated	356
5. 0	150	do	3. 25	22. 4	do	356
2. 5	150	do	3. 30	14. 9	do	356
2. 5	150	Open	3. 4	14. 1	Small	49
2. 5	150	do	3. 30	18. 25	do	111
2. 5	150	do	3. 1	15. 5		104

Downward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7. 5	150	Closed	3. 33	15. 5	Half-saturated	356
6. 2	33	Open	3. 4		Saturated	95
6. 0	120		3. 45	14. 7	Partly dried	325
5. 0	150	Closed	3. 42	15. 3	Half-saturated	356
4. 0	16	do	4. 0	14. 5		124
2. 5	150	do	3. 45	13. 7	Half-saturated	356
2. 5	150	Open	3. 6	13. 7	Small	49
1. 9	40	Closed	4. 1	14. 6	Saturated	95
1. 9	40	do	3. 9	14. 1	do	325
1. 6	30	do	3. 1	14. 1	Dried	217

Influence of Temperature.— Of two sets of observations (12, 358) on the influence of temperature, one appears to be reliable (358). The determinations were made in a closed tube 2.5 cm. in diameter and 150 cm. in length, with downward propagation of flame. The lower limit decreased linearly from 3.45 percent ethylene at about 17° C. to 2.50 percent at 400° C. The higher limit increased from 13.7 percent at about 17° C. to 17.9 percent at 300° C.; the rate of increase became greater as the temperature was increased.

Influence of Impurities.— The lower limit of ethylene in air was scarcely affected by small quantities of iron carbonyl. The higher limit was reduced from 14.7 to 12.4 percent by iron

carbonyl (0.03 cc. liquid vaporized per liter) (325).

ETHYLENE IN OXYGEN

The limits of ethylene in oxygen with upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, are 3.19 and 79.9 percent (173), 2.90 and 79.9 (163).

Table 22 summarizes other determinations of the limits of ethylene in oxygen.

Influence of Pressure.— Certain ethylene-oxygen mixtures are still flammable at 30 mm. pressure (65). This is confirmed (193), and two small irregularities are shown on the higher-limit branch of the diagram showing the relation between pressure and limits.

TABLE 22.—*Summary of other determinations of limits of ethylene in oxygen*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
10. 2	96	Closed	2. 90		Small	183

Downward Propagation of Flame

4	16	Closed	5	[1] 70		124
2		do	3. 4	63		243
		Water-sealed	3. 4	77. 5	Saturated	846
1. 4		Closed	4. 1	60. 2		202

[1] The presence of 5 percent of carbon dioxide reduces this figure to 55.
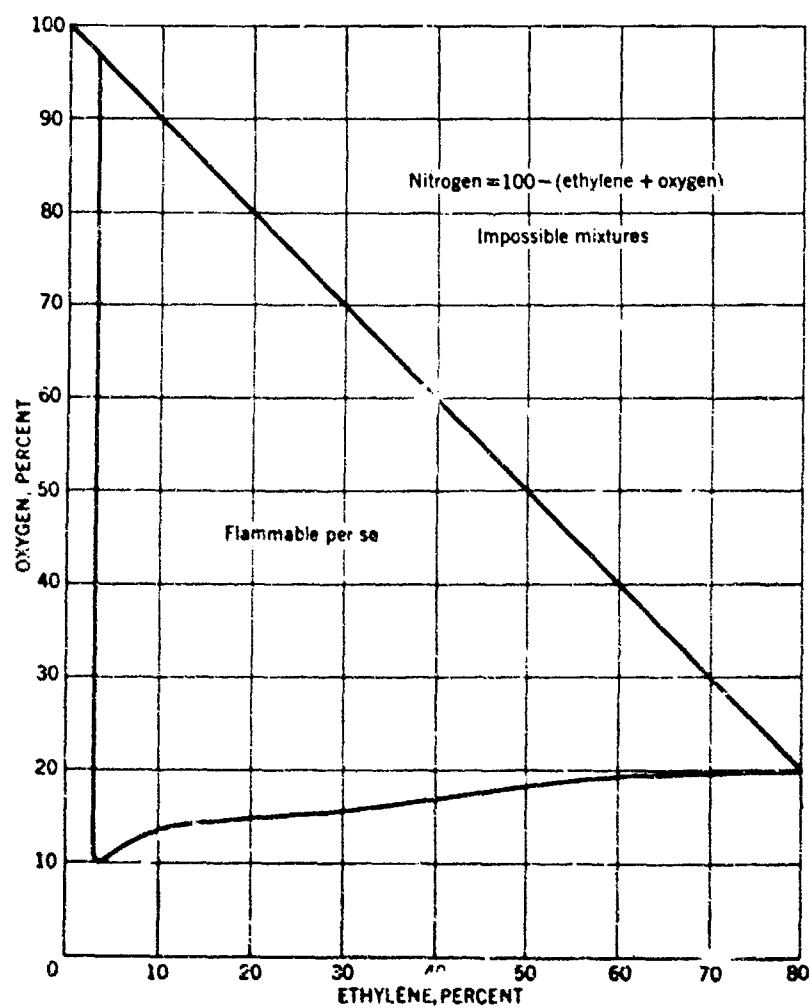
FIGURE 39.—Flammability of Ethylene-Oxygen-Nitrogen Mixtures.

Influence of Impurities.—The addition of small quantities of nitric oxide to various mixtures of ethylene and oxygen reduces the minimum ignition pressure and may, therefore, widen the range of flammability (*104*).

ETHYLENE IN OTHER ATMOSPHERES

All Atmospheres of Oxygen and Nitrogen.—The composition of all flammable mixtures of ethylene, oxygen, and nitrogen is shown in figure 39. The determinations were made in a 2-inch-diameter tube, open at the lower end, with upward propagation of flame (*163*).

Atmospheres of Composition Between Air and Pure Oxygen.—The lower limit of ethylene, for downward propagation of flame in a Bunte burette 1.9 cm. in diameter, increased slightly as the oxygen in the atmosphere was increased to 94 percent; the higher limit rose gradually from 14.1 percent in air to 47.6 in a 60-percent oxygen mixture and to 62 in a 94-percent oxygen mixture (*323*).

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of ethylene in all mixtures of air and nitrogen, or air from which part of the oxygen has been removed, are shown in figure 40. The determinations were made with upward propagation of flame in a tube 2 inches in diameter and 6 feet in length, open at the firing end (*144*).

Atmospheres of Air and Carbon Dioxide.—The limits of ethylene in all mixtures of air and carbon dioxide are shown in figure 40. The determinations were made as described in the previous paragraph.

Some earlier observations (*95*) show, as might be expected, more rapid narrowing of the limits in a Bunte burette.

The limits for downward propagation of flame in a tube 1.6 cm. in diameter have been recorded (*217*).

Atmospheres of Air, Nitrogen, and Carbon Dioxide.—The limits with downward propagation of flame in a tube 1.6 cm. in diameter have been given (*217*).

Atmospheres of Air and Methyl Bromide.—The addition of increasing amounts of methyl bromide to the air causes the limits of ethylene to approach and, in a 2-inch-diameter tube, to meet when 11.65 percent of methyl bromide is present. The lower limit of ethylene is, however, appreciably reduced (down to 1.95 percent with 10.5 percent of methyl bromide), showing that the bromide takes some part in the combustion (*38*). (For a comment, compare the corresponding paragraph on hydrogen, p. 22.)

Atmospheres of Carbon Dioxide and Oxygen.—The limits of ethylene in a carbon dioxide-oxygen atmosphere were given in some old experiments of doubtful accuracy (*346*). (See *also* a footnote to table 22.)

Dilution of $C_2H_4 + 3O_2$ With Gases, Inert or Otherwise.—The following results were obtained with downward propagation of flame in a Bunte burette 1.9 cm. in diameter (*95*):

Effect of diluents upon flammability of $C_2H_4 + 3O_2$

Amount of $C_2H_4 + 3O_2$ which, with diluent named, is present at limit of flammability, percent

Diluent:
Oxygen _____ 15.4
Nitrogen _____ 18.5
Carbon dioxide _____ 22.1

Atmospheres of Oxygen and Helium.—The composition of all flammable mixtures of ethylene, oxygen, and helium is given by a curve almost identical with that of figure 39, except that the "nose" of the curve is at 8.5 percent oxygen (*163*).

Atmosphere of Nitrous Oxide.—The limits of ethylene in nitrous oxide, with upward propagation of flame in a 2-inch-diameter tube open at the lower end, are 1.90 and 40.2 percent (*163*).

With downward propagation of flame in a closed tube 4 cm. in diameter and 16 cm. in length, the limits are 5 and 35 percent. The presence of 10 percent of oxygen raises the higher limit to 47 percent (*124*).

Atmospheres of Oxygen and Nitrous Oxide.—The lower limit of ethylene in mixtures of oxygen and nitrous oxide falls slightly as the

FIGURE 40.—Limits of Flammability of Ethylene in Air and Carbon Dioxide or Nitrogen.

percentage of nitrous oxide rises to 50, then more rapidly as it rises to 100 (*163*).

PROPYLENE

PROPYLENE IN AIR

The limits of propylene in air, with upward propagation of flame in a 2-inch-diameter tube open at its lower end, are 2.40 and 10.3 percent (*151*).

PROPYLENE IN OTHER ATMOSPHERES

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of propylene in all mixtures of air and nitrogen are shown by one of the curves of figure 41. The determinations were made in a 2-inch-diameter tube, open at the lower end, with upward propagation of flame. No mixture of propylene, air, and nitrogen is flammable if it contains less than 11.5 percent of oxygen (*151*).
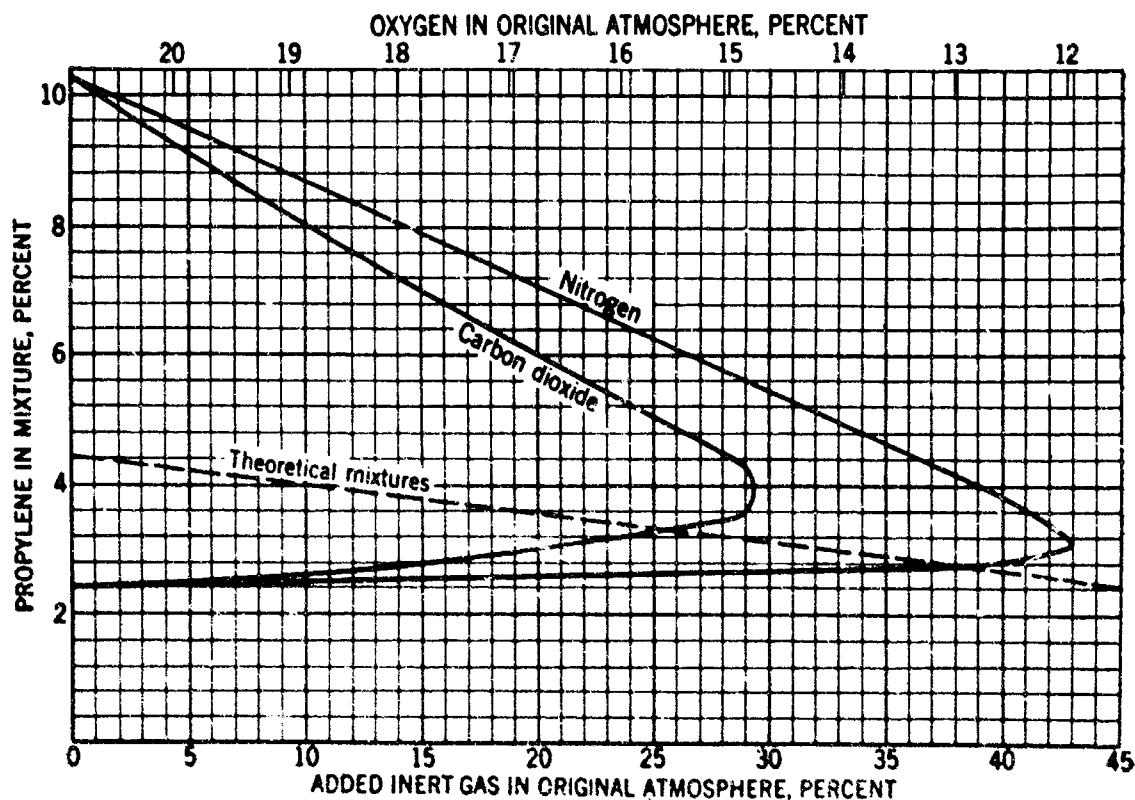
FIGURE 41.—Limits of Flammability of Propylene in Mixtures of Air and Added Nitrogen and Carbon Dioxide.

Table 23 gives other determinations of the limits.

PROPYLENE IN OXYGEN

The limits of propylene in oxygen with upward propagation of flame in a tube 2 inches in diameter, open at its lower end, are 2.10 and 52.8 percent (*144, 150*).

Atmospheres of Air and Carbon Dioxide.—Figure 41 also shows the limits of propylene in all mixtures of air and carbon dioxide, determined as in the previous paragraph (*151*).

Atmosphere of Nitrous Oxide.—The limits of propylene in nitrous oxide, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are 1.45 and 28.8 percent (*163*).

TABLE 23.—*Summary of other determinations of limits of flammability of propylene in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
1C. 2	96	Closed..	2. 00	11. 1	Dried	*150*
7. 5	150	do	2. 18	9. 7	Half-saturated	*356*
5. 0	150	do	2. 21	9. 6	do	*356*

Horizontal Propagation of Flame

7. 5	150	Closed	2. 22	9. 3	Half-saturated	*356*
5. 0	150	do	2. 26	8. 4	do	*356*
2. 5	150	Open	2. 6	7. 4	Small	*49*
2. 5	150	do	2. 58	7. 5	do	*111*

Downward Propagation of Flame

7. 5	150	Closed	2. 26	7. 4	Half-saturated	*356*
5. 0	150	do	2. 29	7. 2	do	*356*

BUTYLENES

The limits of the various butylenes in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are (*138*):

	Percent	
"Butylene"	1. 98 and	9. 65
Butene-1	1. 65	9. 35
Butene-2	1. 85	9. 70
Isobutylene	1. 78	8. 85

Table 24 gives other determinations of the limits of "butylene."

AMYLENE

The limits of *b–n*–amylene in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 1.50 and 8.70 percent (*138*).

TABLE 24.—*Other determinations of limits of butylene in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7. 5	150	Closed	1. 70	9. 0	Half-saturated	*356*
5. 0	150	do	1. 80	9. 0	do	*356*

Horizontal Propagation of Flame

7. 5	150	Closed	1. 77	9. 0	Half-saturated	*356*
5. 0	150	do	1. 82	7. 4	do	*356*
2. 5	150	Open	1. 93	6. 0	Small	*111*

Downward Propagation of Flame

7. 5	150	Closed	1. 80	6. 25	Half-saturated	*356*
5. 0	150	do	1. 84	6. 10	do	*356*

The lower limit of amylene in air, apparently with downward propagation of flame in a 2-liter bottle, is 1.6 percent (*221*).

BUTADIENE

BUTADIENE IN AIR

The limits of butadiene in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 2.0 and 11.5 percent (*152, 153*).

BUTADIENE IN OTHER ATMOSPHERES

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of butadiene in all mixtures of air and nitrogen are shown by one of the curves of figure 42. The determinations were made in a 2-inch-diameter tube, open at the lower end, with upward propagation of flame. No mixture of butadiene, air, and nitrogen is flammable if it contains less than 10.4 percent of oxygen (*153*).

Atmospheres of Air and Carbon Dioxide.—Figure 42 also shows the limits of butadiene in all mixtures of air and carbon dioxide, determined as in the previous paragraph (*153*).

ACETYLENE

ACETYLENE IN AIR

The lower limit of acetylene in air with upward propagation of flame in a tube 5 cm. in diameter and 150 cm. in length, open at the firing end, is 2.50 percent (*150*).

In a box about 4.6 feet high and 12 inches square in cross section the lower limit for propagation of flame upward toward the open top was 2.53 percent acetylene (*44*). In a bell jar, with turbulence, the figure was 2.30 (*138*).

With downward propagation of flame in the box, presumably toward the closed end, the lower limit was about 2.8 percent (*44*). An earlier determination in a 90-liter vessel 41 cm. in diameter and 89 cm. in height gave the limits as 3 and 80 percent acetylene (*112*).

Table 25 gives other determinations of the limits.

Where a range is given for the higher-limit figures in table 25, the experimental result depended on the state of the walls of the container (*261*).

Limits in vessels other than tubes were as follows: In an 84-liter bomb, 2.4 and 80 percent (*113*); in a 2.8-liter bottle for central ignition,
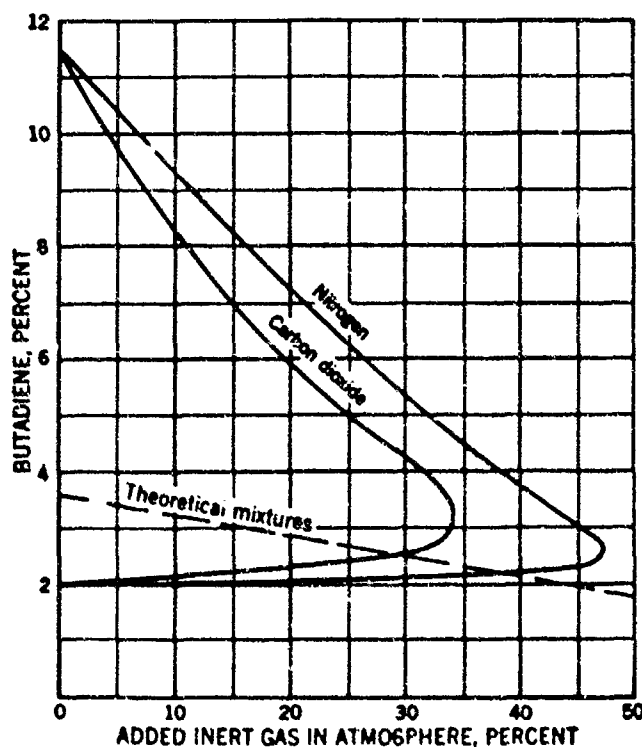
FIGURE 42.—Limits of Flammability of Butadiene in Mixtures of Air and Nitrogen, and of Air and Carbon Dioxide.

3.0 and 73 percent (*44*); in a 2-liter rubber balloon with flame ignition, 75 percent (higher limit) (*95*); in a 100-cc. Hempel pipette with downward propagation of flame, 2.9 and 51 percent (*44*) and 2.45 and 57.05 percent (*364*); in a small vessel, 2.3 and 73.4 percent (*9*).

A few experiments have been reported on the "flammability of acetylene mixed with about 30 percent of air," but this mixture is well within the limits of flammability, and the report (*81*) is concerned only with conditions for ignition.

TABLE 25.—*Summary of other determinations of limits of flammability of acetylene in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed	2.60	>80.5	Half-saturated	*356*
5.0	150	do	2.60	78	do	*356*
5.0	30.6	do	2.4	78	Saturated	*176*
2.5	150	do	2.73	70	Half-saturated	*356*
2.5			3.03	54–63.0		*261*
2.0			3.07	51–62.8		*261*
1.5			3.09	48–62.2		*261*
1.0				45–61.4		*261*

Horizontal Propagation of Flame

7.5	150	Closed	2.68	>78.5	Half-saturated	*356*
5.0	150	do	2.68	68.5	do	*356*
2.5	150	do	2.87	59.5	do	*356*
2.5			3.25	54–62.7		*261*
2.0			3.25	51–62.4		*261*
1.5			3.25	48–61.1		*261*
1.0				45		*261*

Downward Propagation of Flame

12.2	21	Open		75	Saturated	*95*
10.0	13	do		70	do	*95*
7.5	150	Closed	2.78	71.0	Half-saturated	*356*
5.0	150	do	2.80	63.5	do	*356*
4.4	26	Open		60	Saturated	*95*
2.5	150	do	2.90	55.0	Half-saturated	*356*
2.5			3.17	53–62.1		*261*
2.0			3.20	49–60.7		*261*
1.9	40	Open	3.45	52.2	Saturated	*95*
1.9	40	do	3.45	52.4	do	*323*
1.5			3.24	45–58.3		*261*
1.0				41–53.7		*261*

Direction of Flame Not Stated

4.0			2.9	64		*219*
3.0			3.1	62		*219*
2.0			3.5	55		*219*
.6			4.0	40		*219*
.4			4.5	25		*219*
.2			5.0	15		*219*
.05			7.7	10		*219*
.05			No propagation			*219*

Influence of Pressure.—The lower limit in a Hempel pipette was unchanged by increase of pressure to 5 atmospheres (44).

The higher limit, observed in a closed 2-inch-diameter tube at 24° C. with mixtures saturated with water vapor, rose almost linearly from 78 to 100 percent as the pressure was raised from atmospheric to 7 pounds per square inch above atmospheric (176). The flammability of the richer mixtures is evidently assisted by the exothermic decomposition of much of the acetylene that is not burned, and the 100 percent acetylene transmits flame by this means entirely. A source of ignition developed locally in a generator may thus cause explosion of the gas at pressures attainable in medium-pressure generators, even in the absence of air (176). The addition of water vapor raises proportionately the minimum pressure for explosion of acetylene and of rich acetylene-air mixtures. Propane, butane, and natural gas have similar effects, in differing degrees (158). Nitrogen, helium, and hydrogen have less effect than the hydrocarbons named, and carbon dioxide is intermediate in its effect (159).

The effect of reduced pressure on the limits of ignitibility of acetylene in air by a weak standard spark, rather than on its limits of flammability, have been examined (8).

Influence of Temperature.—The lower limit, with downward propagation of flame in a closed tube 2.5 cm. in diameter and 150 cm. in length, decreased linearly from 2.90 percent at about 17° C. to 2.19 percent at 300° C. The higher limit increased from 55 percent at about 17° C. to somewhat over 81 percent at 200° C. (358).

In an older observation (95) the higher limit, with downward propagation of flame from the open end of a cylinder 4.4 cm. in diameter and 26 cm. in length, was 60 percent acetylene at laboratory temperature and 75 percent at 200° C.

ACETYLENE IN OXYGEN

An old experiment gave the higher limit of acetylene in oxygen, with downward propagation of flame, as 83 percent acetylene (243). An estimate for "an infinite mass" (not cooled by the walls of a container) gave limits of 2.8 and 93 percent (219).

The lower limit for downward propagation of flame in a Bunte burette, 1.9 cm. in diameter, is 3.1 percent acetylene (95). The limits in a Hempel pipette are 2.45 and 89.2 percent (364).

ACETYLENE IN OTHER ATMOSPHERES

Atmospheres of Composition Between Air and Pure Oxygen.—The lower limit of acetylene, with downward propagation of flame in a

Bunte burette 1.9 cm. in diameter, was unchanged as the oxygen in the atmosphere was increased to 97 percent; the higher limit rose gradually from 52.4 percent in air to 82.2 in 58 percent oxygen and to 89.7 in 96.8 percent oxygen (323).

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—In an 84-liter bomb, the lower limit of acetylene rose slightly with increasing additions of nitrogen to the atmosphere while the higher limit fell rapidly. From limits of 2.4 and 80 percent in pure air, the limits met at 2.75 percent in an atmosphere containing 69 percent of "added" nitrogen. At this point about 6.5 percent of oxygen is present, in comparison with about 4 percent at the higher limit in air (113). In a Hempel pipette the lower limit rose from 2.45 percent in air to 3.3 percent in an atmosphere containing 8.7 percent oxygen; at the higher limit the oxygen in the mixture was constant at about 11 percent except that close to the point where the limits met it fell to 8 percent (364).

Atmospheres of Air and Carbon Dioxide.—In an 84-liter bomb, the lower limit of acetylene rose slightly with increasing additions of carbon dioxide to the atmosphere while the higher limit fell rapidly. From limits of 2.4 and 80 percent in pure air, the limits met at 3.75 percent in an atmosphere containing 55 percent of carbon dioxide. At this point about 9 percent of oxygen is present (113). In a Bunte burette no flammable mixture could be made in an atmosphere containing 46 percent of carbon dioxide (11.5 percent of oxygen) (95).

Atmospheres in Which Oxygen of the Air Is Replaced by Carbon Dioxide.—A few experiments in a Bunte burette show the narrowing of the range of flammable mixtures by the gradual replacement of the oxygen of the air by carbon dioxide. No flammable mixture could be made when the oxygen was reduced to 8 percent (carbon dioxide, 13 percent) (95).

Atmospheres of Air and Certain Chlorinated Hydrocarbons.—Limits of acetylene in air containing vapors of various chloro-derivatives of hydrocarbons have been reported; they were observed in small burettes 15 mm. in diameter, so are of limited value (198).

Atmosphere of Nitrous Oxide.—The limits of acetylene in nitrous oxide, with downward propagation of flame in a 16-mm. burette, are 2.2 and 67.0 percent. The effect of helium in narrowing the limits is greater than that of argon (285).

Dilution of $2C_2H_2 + 5O_2$ With Gases, Inert or Otherwise.—The following results were obtained with downward propagation of flame in a Bunte burette 1.9 cm. in diameter (95).

Effect of diluents upon flammability of
$$2C_6H_6+5O_2$$

Diluent:	Amount of $2C_6H_6+5O_2$ which, with diluent named, is present at limit of flammability, percent
Oxygen	10. 9
Nitrogen	13. 0
Carbon dioxide	18. 7

BENZENE

BENZENE IN AIR

The limits of benzene in air, with upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, are 1.40 and 7.10 percent (136) and 1.55 percent (lower limit only) (31).

Table 26 summarizes other determinations of the limits of benzene in air.

The lower limits in a 5-cm. tube closed at both ends differed only in the second decimal place from those obtained when a small stopcock was opened at one end or the other. Similar differences were observed when the length of tube was varied between the limits of 100 and 250 cm. and when the position of the point of ignition was brought forward about 6 cm. (353).

Influence of Pressure.—The range of flammability of benzene in air is widened at both sides by an increase in pressure above atmospheric, provided the temperature is raised to maintain enough vapor for the test. This effect

TABLE 26.—*Summary of other determinations of limits of flammability of benzene in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
30. 6	39	Vented at top	1. 32		Undried	239
7. 5	150	Closed	1. 41		Dry	353
5. 0	150	...do	1. 45	[1] 7. 45	...do	353
5. 0	91	...do	1. 50	8. 0	...do	351
2. 5	150	...do	1. 55		...do	353
2. 5	25	Central ignition	[2] 1. 5	9. 5	Undried	294

Horizontal Propagation of Flame

7. 5	150	Closed	1. 46		Dry	353
5. 0	150	...do	1. 46	[1] 6. 65	...do	353
5. 0	91	...do	1. 55	6. 5	...do	351
2. 5	150	...do	1. 55		...do	353

Downward Propagation of Flame

7. 5	150	Closed	1. 46		Dry	353
6. 2		Open	1. 4		Saturated	95
6. 0	120		1. 3		Partly dried	325
5. 0	150	Closed	1. 48	[1] 5. 55	Dry	353
5. 0	91	...do	1. 60	5. 0	...do	351
5. 0	65	...do	1. 47	5. 45	...do	316
2. 5	150	...do	1. 58		...do	353
1. 9	40	...do	2. 65	6. 5	Saturated	95
1. 9	40	...do	2. 7	7. 0	...do	323

Propagation in Globes, etc.

Capacity:					
14.5 liters		1. 3			95
350 cc		[1] 1. 7	[2] 8. 3	Saturated	368
Very small vessel		. 8	8. 6		9

[1] At 60° C.
[2] For "99 percent benzene," boiling point 77°-118° C.
[3] Believed to be somewhat on the high rather than the low side.

may be due more to the change in temperature than to that in pressure (*14*).

The effect of reduced pressure on the limits of ignitibility of benzene in air by a standard spark, rather than its limits of inflammability, have been examined (*13*).

Influence of Temperature.—The lower limit of benzene in air for upward propagation in a tube 30.6 cm. in diameter and 39 cm. in length, vented at its upper end, mixture undried, is 1.32 percent at 21° C., 1.10 at 100° C., 0.93 at 200° C., and 0.80 at 300° C. (*239*). The limits of benzene in air for downward propagation of flame in a vessel 9 cm. in diameter and 45 cm. in length widen linearly from 1.37 and 5.32 percent at 100° C. to 1.13 and 5.58 at 250° C. (*21, 22*).

BENZENE IN OTHER ATMOSPHERES

Atmospheres of Composition Between Air and Pure Oxygen.—The lower limit of benzene in a spherical vessel with ignition near the top was unchanged as the oxygen in the atmosphere was increased to 97 percent; the higher limit rose gradually from 7 percent in air to 20.7 in 58 percent oxygen and 30 in 97 percent oxygen (*323*); in a 120-cc. Bunte burette 1.9 cm. in

diameter, ignition by spark and downward propagation of flame, the limits in oxygen were 2.8 and 24.9 percent (*323*).

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of benzene in all mixtures of air and nitrogen are shown by one of the curves of figure 43. The determinations were made in a 2-inch-diameter tube, open at the lower end, with upward propagation of flame. No mixture of benzene, air, and nitrogen is flammable if it contains less than 11.2 percent of oxygen (*136*).

Atmospheres of Air and Carbon Dioxide.—Figure 43 also shows the limits of benzene in all mixtures of air and carbon dioxide, determined as in the previous paragraph (*136*).

Atmospheres of Air and Water Vapor.—The limits of benzene-air mixtures standing over water in a 350-cc. spherical vessel, and ignited near the water surface, have been determined at various temperatures. As the temperature rises (and consequently the water-vapor content also) the lower limit rises slowly, and the higher limit falls rapidly, as with other diluents. When about 35 percent of water vapor is present the limits coincide at about 2.5 percent benzene vapor (*368*).
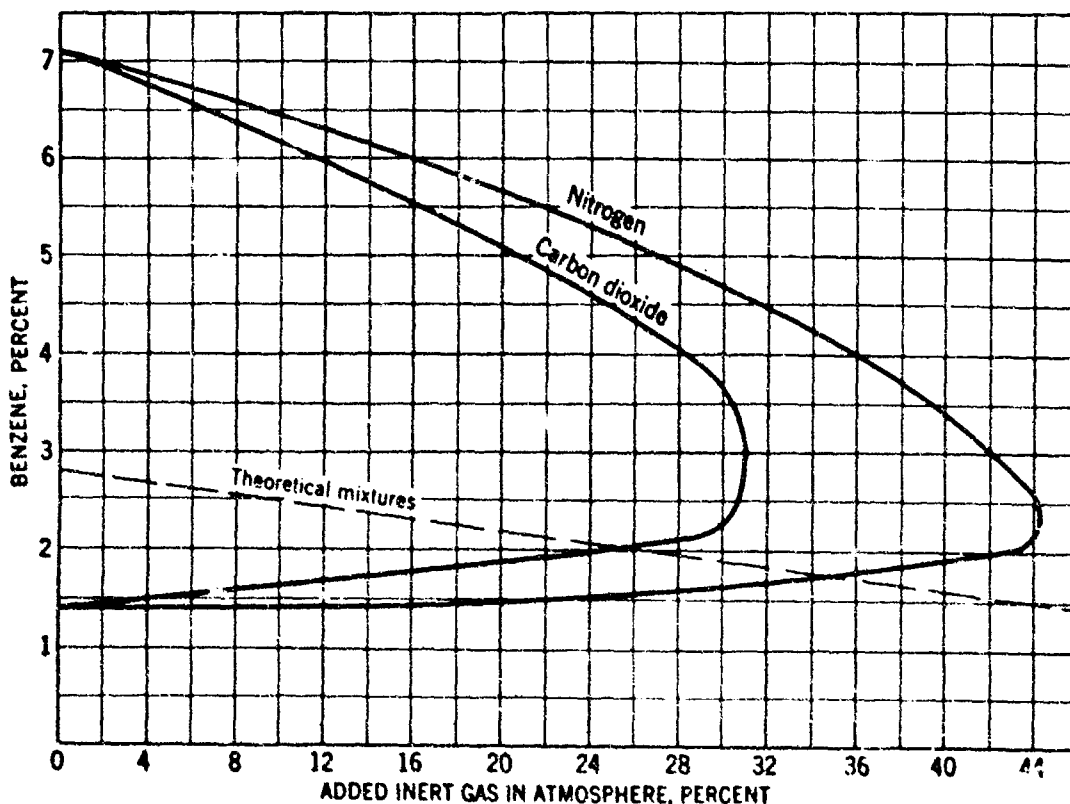
FIGURE 43.—Limits of Flammability of Benzene in Mixtures of Air and Nitrogen, and of Air and Carbon Dioxide.

Atmospheres of Air and Methyl Bromide.—
The addition of increasing amounts of methyl bromide to the air causes the limits of benzene to approach and, in a 2-inch-diameter tube, to meet when 7.75 percent of the mixture is methyl bromide (38). For a comment, compare the corresponding paragraph on hydrogen (p. 22).

TOLUENE

The lower limit of toluene in air, with upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, is 1.45 percent (138) or 1.49 percent (31).

Table 27 summarizes other determinations of the limits of toluene in air.

Earlier experiments gave approximately 1.3 and 1.4 percent for the lower limit, probably with downward propagation of flame (213, 221).

Influence of Temperature.—The limits of toluene in air at 110° C., with upward propagation of flame in a closed tube 5.0 cm. in diameter and 18 inches in length, open at the top, are 1.20 and 7.20 percent, respectively (138).

The lower limit with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39 cm. in length, vented at the upper end, is 0.99 percent at 100° C., 0.82 at 200° C., and 0.72 at 300° C. (239).

The lower limit of toluene in air with upward propagation of flame in a closed tube 10.2 cm. in diameter and 96 cm. in length fell from 1.27 percent at 26° C. to 1.12 at 200° C. (139). The limits for downward propagation of flame in a vessel 9 cm. in diameter and 45 cm. in length widen linearly from 1.26 and 4.44 percent at 100° C. to 1.03 and 4.61 at 200° (21, 22).

TABLE 27.—*Summary of other determinations of limits of flammability of toluene in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
30. 6	39	Vented at top	1. 17		Undried	239
10. 2	96	Closed	1. 27			139
7. 5	150	do	1. 27		Dry	353
5. 0	150	do	1. 31	¹6. 75	do	353
2. 5	25	Central ignition	1. 3	7. 0	Undried	104

Horizontal Propagation of Flame

7. 5	150	Closed	1. 28		Dry	353
5. 0	150	do	1. 30	¹5. 80	do	353

Downward Propagation of Flame

7. 5	150	Closed	1. 28		Dry	353
5. 0	150	do	1. 32	¹4. 60	do	353

¹ At 60° C.

ORTHOXYLENE

The limits of orthoxylene in air, conditions not specified, are reported as 1.0 and 6.0 percent (101).

ETHYL BENZENE

The lower limit of ethyl benzene in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, is 0.99 percent (138).

STYRENE

The limits of styrene in air, with upward propagation of flame in a tube 1 inch in diameter and open at the upper end, are: Lower, 1.10 percent (at 29.3° C.); higher, 6.10 percent (at 65.2° C.) (177).

BUTYL BENZENE

The limits of n-butyl benzene in air, with upward propagation of flame in a 2-inch-diameter tube, open at its upper end and at a

sufficient temperature to volatilize the butyl benzene, are 0.82 and 5.75 percent (*138*); isobutyl benzene, 0.83 and 6.00 percent; sec-butyl benzene, 0.78 and 6.90 percent; and tert-butyl benzene, 0.84 and 5.60 percent (*138*).

DIETHYL BENZENE

The limits of 1,4 diethyl benzene in air, with upward propagation of flame in a tube 2 inches in diameter, 18 inches in length, open at its upper end and at a temperature of 110° C., are 0.80 and 6.10 percent (*138*).

NAPHTHALENE

The limits of naphthalene in air, with upward propagation of flame in a tube 1 inch in diameter and open at its upper end, are: Lower, 0.88 percent (at 77.8° C.); higher, 5.9 percent (at 121.8° C.) (*174*). The lower limit of a cloud of naphthalene dust is about 50 mg. per liter,

which is equivalent to about 0.9 percent of vapor (*242*).

CYCLOPROPANE

CYCLOPROPANE IN AIR

The limits of cyclopropane in air with upward propagation of flame in a 2-inch tube 6 feet in length, open at the lower end, are 2.45 and 10.45 percent (*161*), 2.40 and 10.3 percent (*163*). In an 8-liter bomb with upward propagation of flame, the limits are 2.58 and 10.1 percent (*161*).

CYCLOPROPANE IN OXYGEN

The limits of cyclopropane in oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 2.48 and 60 percent (*161*).

CYCLOPROPANE IN OTHER ATMOSPHERES

All Atmospheres of Oxygen and Nitrogen.— The compositions of all flammable mixtures of
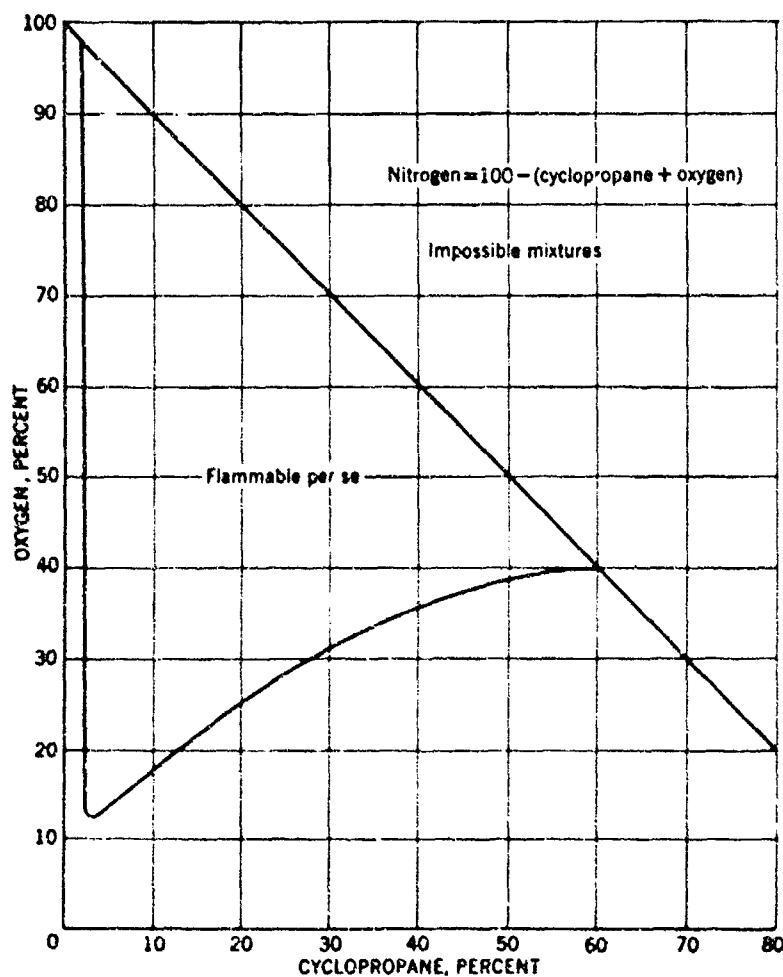
FIGURE 44.—Flammability of Cyclopropane-Oxygen-Nitrogen Mixtures.

cyclopropane, oxygen, and nitrogen are shown in figure 44. The determinations were made in a 2-inch-diameter tube, open at the lower end, with upward propagation of flame (163). The results nearly coincide with those of an earlier series (116) for which, however, the experimental conditions were not stated. No mixture is flammable if it contains less than 11.5 percent oxygen.

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of cyclopropane in all mixtures of air and nitrogen are shown by one of the curves of figure 45. The determinations were made in a 2-inch-diameter tube, open at the lower end, with upward propagation of flame. No mixture of cyclopropane, air, and nitrogen is flammable if it contains less than 11.7 percent of oxygen (161).

Atmospheres of Air and Carbon Dioxide.—Figure 45 also shows the limits of cyclopropane in all mixtures of air and carbon dioxide, determined as in the previous paragraph (161).

Atmospheres of Air and Helium.—Figure 45 also shows the limits of cyclopropane in all mixtures of air and helium (161).

The relative effects of nitrogen, carbon dioxide, and helium on the limits of cyclopropane are similar to their effects on the limits of methane and support the explanation given in the corresponding paragraphs on methane.

Atmospheres of Oxygen and Helium.—The composition of all flammable mixtures of cyclopropane, oxygen, and helium is given by a curve almost identical with that of figure 44, except that the "nose" of the curve is at 10 percent oxygen (161. 163).

Atmosphere of Nitrous Oxide.—The limits of cyclopropane in nitrous oxide, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 1.60 and 30.3 percent (163).

Atmospheres of Oxygen and Nitrous Oxide.—The compositions of all flammable mixtures of cyclopropane, oxygen, and nitrous oxide are
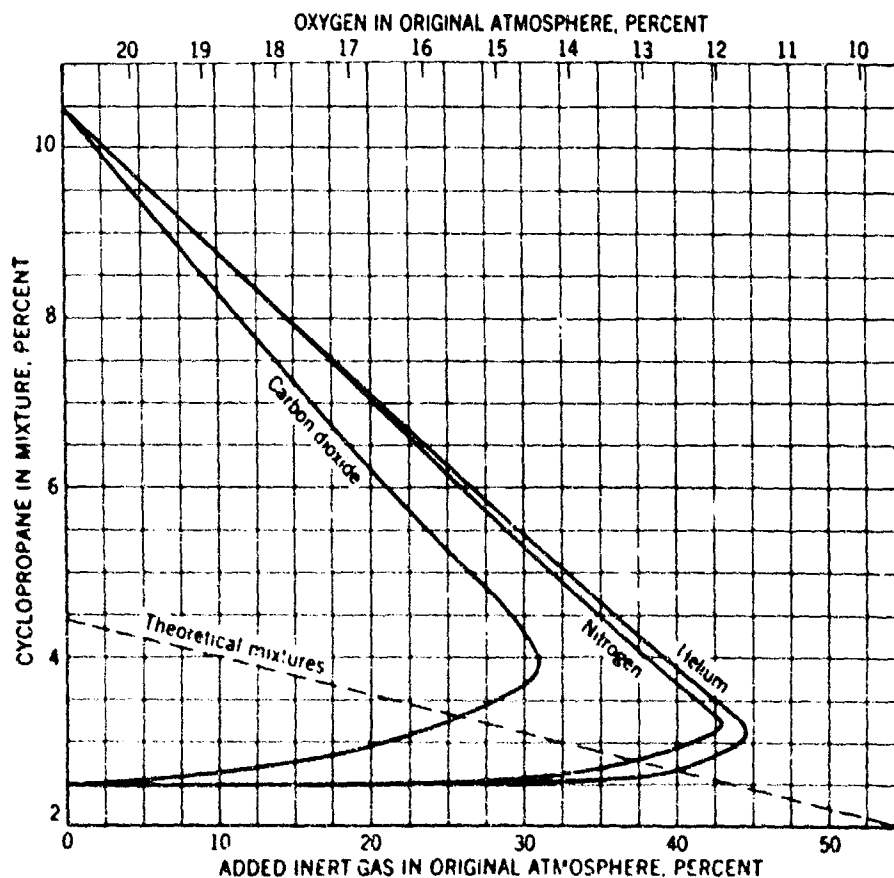
FIGURE 45.—Limits of Flammability of Cyclopropane in Mixtures of Air and Nitrogen, Air and Helium, and Air and Carbon Dioxide.

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FIGURE 47. Flammability of Cyclopropane-Nitrous Oxide-Helium Mixtures.

Influence of Temperature.—The limits of cyclohexane in air, with downward propagation of flame in a vessel 9 cm. in diameter and 45 cm. in length, widen linearly from 1.16 and 4.34 percent at 100° C. to 0.95 and 4.98 at 250° C. (21, 22).

The lower limit in air with upward propagation of flame in a cylinder 30.6 cm. in diameter and 59 cm. in length, vented at its upper end, is 1.12 percent at 21° C., 1.01 at 100° C., and 0.83 at 200° C. (239).

CYCLOHEXANE IN OTHER ATMOSPHERES

Atmosphere of Air and Methyl Bromide.—The addition of increasing amounts of methyl bromide to the air causes the limits of cyclohexane to approach and, in a 2-inch-diameter tube, to meet when 7.4 percent of the mixture is methyl bromide (38). (For a comment, compare the corresponding paragraph on hydrogen, p. 22.)

METHYL CYCLOHEXANE

The lower limit of methyl cyclohexane in air, in a tube 5 cm. in width, is 1.25 percent with upward propagation of flame (31) and 1.15 percent with downward propagation (246). For the former observations the tube was open at the firing end; for the latter it was partly opened (by stopcocks) at both ends.

Influence of Impurities.—The lower limit was unaffected by small additions of diethyl selenide or lead tetraethyl. The effects of pyridine and diethyl selenide agreed with Le Chatelier's formula (252).

ETHYL CYCLOHEXANE

The limits of ethyl cyclohexane in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 0.95 and 6.60 percent at (138).

CYCLOHEXENE

Temperatures Above Normal.—The limits of cyclohexene in air, with downward propagation of flame in a vessel 9 cm. in diameter and 45 cm. in length, widen linearly from 1.22 and 4.81 percent at 100° C. to 0.96 and 5.20 at 250° C. (*21, 22*).

METHYL ALCOHOL

METHYL ALCOHOL IN AIR

The lower limit of methyl alcohol in air, with upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, is 7.35 percent (*138*).

Table 28 summarizes other determinations of the limits of methyl alcohol in air.

The lower limit in a 2-liter flask, with ignition near the base, is 6.1 percent (*76*). Two older figures (*213, 221*), probably with downward propagation of flame, are 6 and 7.8 percent.

Influence of Temperature.—Of two series of experiments on the influence of temperature on the limits of methyl alcohol (*230, 365*), the latter, which seem to be reliable, show that, with downward propagation of flame in a 2½-liter bottle, the lower limit falls steadily from 7.5 percent at 50° to 5.9 at 250° C. The higher

limit rises from 24.9 percent at 100° to 36.8 at 200° C.

The lower limit in air with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39 cm. in length, vented at the top, is 6.70 percent at 21° C., 5.80 at 100° C., 4.81 at 200° C., 4.62 at 250° C., and 4.44 at 300° C. (*239*).

In another series of experiments the lower limit fell from 6.65 percent at 100° C. to 5.45 at 250° C. (*21, 23*).

Influence of Water.—The lower limits of mixtures of methyl alcohol and water rise steadily as the quantity of water is increased from 0 to 60 percent by weight, but the amount of methyl alcohol itself is approximately constant in the limit mixture. With 80 percent water it was difficult to inflame any mixture of the vaporized liquid and air at 105° C., and 85 percent water made inflammation virtually impossible (*230*).

Influence of Pressure.—Reduction of pressure below atmospheric reduces slightly the lower limit of flammability of methyl alcohol in air but has a marked effect on the higher limit (*171a*). The lowest pressure at which any mixture propagated a flame from the bottom to the top of a tube 2 inches in diameter and 5 feet in length, with spark ignition, was 50 mm. The minimum pressure mixture contained 9.07 percent of alcohol vapor. When ignition was

TABLE 28.—*Summary of other determinations of limits of flammability of methyl alcohol in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
30. 6	39	Vented at top	6. 70		Undried	*239*
10. 2	96	Closed	6. 72		Dry	*138*
7. 5	150	do	7. 05		do	*353*
5. 0	150	do	7. 10	¹ 36. 5	do	*353*
5. 0	91	do	6. 0		do	*351*
2. 5	150	do	7. 9		do	*353*
2. 5	25	Central ignition	5. 5	21. 0	Undried	*294*

Horizontal Propagation of Flame

7. 5	150	Closed	7. 30		Dry	*353*
5. 0	150	do	7. 35	¹ 30. 5	do	*353*
5. 0	91	do	6. 40	13. 50	do	*351*
2. 5	150	do	7. 9		do	*353*

Downward Propagation of Flame

7. 5	150	Closed	7. 45		Dry	*353*
5. 0	150	do	7. 65	¹ 26. 5	do	*353*
5. 0	91	do	6. 80		do	*351*
2. 5	150	do	8. 0		do	*353*

¹ At 60° C.

brought about by fusion of a platinum wire in contact with 1 mg. of guncotton, certain mixtures propagated flames at as low as 26 mm. pressure (171a).

METHYL ALCOHOL IN OTHER ATMOSPHERES

Atmospheres of Nitrogen and Oxygen and of Carbon Dioxide and Oxygen.—The limits of methyl alcohol in "atmospheres" of nitrogen and oxygen and of carbon dioxide and oxygen containing 20.9 percent or less oxygen have been determined in a 2-liter flask, with ignition near the base. Curves extending as far as could be determined at laboratory temperatures are given in the original paper. When the oxygen content of a nitrogen-oxygen "atmosphere" was below 10.3 percent, no mixture with methyl alcohol would propagate flame (76).

Atmospheres of Air and Carbon Dioxide.—The limits of methyl alcohol in mixtures of air and carbon dioxide, with downward propagation of flame in a 2-liter cylinder, approach each other as the proportion of carbon dioxide is increased. With more than 26 percent carbon dioxide in the "atmosphere" no mixture with methyl alcohol will propagate flame under these conditions (230).

ETHYL ALCOHOL

ETHYL ALCOHOL IN AIR

The lower limit of ethyl alcohol in air, with upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, is 4.25 (138) or 4.40 percent (31).

Table 29 summarizes other determinations of the limits of ethyl alcohol in air.

TABLE 29.—*Summary of other determinations of limits of flammability of ethyl alcohol in air*

Upward Propagation of Flame

Diameter	Length	Firing end	Far end	Lower	Higher	Content of aqueous vapor	Reference No.
30.6	39 (iron)	Closed	Open	3.48		Undried	239
15	300 (iron)	do	do	4.16		Dry	361
10.2	96 (iron)	do	Closed	3.28			139
7.5	150 (glass)	do	do	3.56		Dry	353
5	150 (glass)	do	Open	4.21	18.95	do	361
5	150 (glass)	do	Closed	3.69	18.00	do	351
5	91 (glass)	do	do	4.30		do	353
2.5	150 (glass)	do	Open	5.02		do	361
2.5	25 (glass)	Central ignition	Closed	5.0	14.0	Undried	294

Horizontal Propagation of Flame

Diameter	Length	Firing end	Far end	Lower	Higher	Content of aqueous vapor	Reference No.
15	300 (iron)	Closed	Open	4.23		Dry	361
7.5	150 (glass)	do	Closed	3.70		do	353
5	150 (glass)	do	Open	4.32	13.80	do	361
5	150 (glass)	do	Closed	3.75	13.80	do	353
5	91 (glass)	do	do	4.40		do	351
2.5	150 (glass)	do	Open	5.18		do	361

Downward Propagation of Flame

Diameter	Length	Firing end	Far end	Lower	Higher	Content of aqueous vapor	Reference No.
15	300 (iron)	Closed	Open	4.37		Dry	361
7.5	150 (glass)	do	Closed	3.75		do	353
6.2	33 (glass)	Open	do	3.70		Saturated	95
5	150 (glass)	Closed	Open	4.44	11.50	Dry	361
5	150 (glass)	do	do	3.78	11.50	do	353
5	91 (glass)	do	Closed	4.50		do	351
5	70 (glass)	Partly open	Partly open	3.81		do	319
2.5	150 (glass)	Closed	Open	5.21		do	361
1.9	40 (glass)	do	Closed	3.95	13.65	Saturated	95
Heated pipette		do	do	5.0	11.5		83

1 At 60° C.

The limits in a small vessel have been stated as 2.6 and 9.0 percent (9); in an upright closed tube of 1,400 cc. capacity, with 600 cc. of liquid at the bottom and central ignition, the limits were 3.2 percent (saturation of the atmosphere at 10.6° C.) and 18.9 percent (saturation at 41.2° C.) (109).

Influence of Pressure.—Curves showing the influence of pressures up to 500 atmospheres have been given (11), but the range of flammability shown seems impossibly wide.

The effect of reduced pressure on the limits of ignitibility of ethyl alcohol in air by a weak standard spark, rather than on its limits of flammability, have been examined (8).

Influence of Temperature.—The lower limit of ethyl alcohol in air, with upward propagation of flame in a tube 5 cm. in diameter, is 4.25 percent at laboratory temperature (138) and 3.85 percent at 125° C. (164). Four other series of observations have been recorded (20, 23, 280, 365). The fourth set, which seems reliable, shows that, with downward propagation of flame in a 2½-liter bottle, the lower limit falls steadily from 3.80 percent at 50° to 2.75 at 225° C. At 250° C. the lower limit rose to 3.05 percent, but this increase presumably was due to slow combustion of part of the mixture before ignition. The lower limit found later in the same apparatus fell from 3.55 percent at 100° C. to 2.75 percent at 250° C. (21, 23).

In a recent series of experiments, the lower limit in air with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39 cm. in length, vented at the top, mixtures undried, is 3.48 percent at 21.° C., 3.01 at 100° C., 2.64 at 200° C., 2.47 at 250° C., and 2.29 at 300° C. (289).

Influence of Pressure and Temperature Together.—The limits of ethyl alcohol in air, determined in a cylindrical steel bomb of 700 cc. capacity after heating under pressure for 30 to 45 minutes to allow preflame combustion to occur, are shown in table 30. The limits are expressed in percentages by weight; the range widens at first with increase of temperature but narrows when preflame combustion becomes evident, as was shown by chemical analysis of

samples. The bomb was filled at atmospheric temperature to an initial pressure of 5.8 atmospheres (245).

The lower-limit figures are unexpectedly high, when compared with the lower limit at atmospheric pressure and temperature. This is perhaps due to the use of too weak a spark for ignition, as suggested by the observation that at 270° C. violent explosions resulted from spontaneous ignition of mixtures containing upward of 6.9 percent by weight of ethyl alcohol.

Influence of Impurities.—The lower limit of ethyl alcohol in air was unaffected by small additions of water vapor, diethyl selenide, or lead tetraethyl. The effect of a little pyridine agreed with Le Chatelier's formula (252).

Influence of Water.—The lower limits of mixtures of ethyl alcohol and water rise steadily as the amount of water increases from 0 to 60 percent by weight, but the amount of ethyl alcohol itself is approximately constant in the limit mixture. With 80 percent water it was difficult to inflame any mixture of the vaporized liquid and air at 105° C., and 85 percent water made inflammation virtually impossible (230).

More recent results, with downward propagation of flame in a closed bottle of 2½ liters capacity at 150° C., are as follows (21):

Limits of mixtures of ethyl alcohol and water in air, downward propagation of flame at 150° C.

Water in liquid mixture, percent by volume	Lower limit, percent		Higher limit, percent	
	Ethyl alcohol vapor	Water vapor	Ethyl alcohol vapor	Water vapor
0	3.15	0	11.80	0
33.0			9.95	15.0
53.0			8.90	26.0
63.0	3.50	17.0		
68.5			7.55	36.5
78.5	4.10	33.5	....	....
80.5	4.90	41.0	....	....

ETHYL ALCOHOL IN OTHER ATMOSPHERES

Atmospheres of Air and Carbon Dioxide.—The limits of ethyl alcohol in mixtures of air and carbon dioxide, with downward propagation of flame in a 2-liter cylinder, approach each other as the proportion of carbon dioxide is increased. With more than 36 percent carbon dioxide in the "atmosphere" no mixture with ethyl alcohol will propagate flame under these conditions (230).

Atmospheres of Air and Trichloroethylene.—The limits of mixtures of ethyl alcohol and trichloroethylene in air, in a Hempel pipette, gradually approach each other as the proportion of trichloroethylene is increased; when the liquid (which is completely evaporated) contains more than 75 percent by volume trichloroethylene no flammable mixture can be made (83).

TABLE 30.—*Limits of ethyl alcohol in air at increased pressures and temperatures*

Temperature, ° C.	Pressure	Limits (percent by weight)	
		Lower	Higher
210	Not stated	20.6	36.0
220	do	18.9	35.8
240	do	19.8	34.8
245	do	20.6	33.8
290	do	21.6	(¹)

¹ Spontaneous inflammation.

PROPYL ALCOHOL

The limits of n-propyl alcohol in air, with upward propagation of flame in a closed bomb 4 inches in diameter and 38 inches in length, at a temperature sufficient to vaporize the alcohol, are 2.15 and 13.50 percent (138).

Older determinations of the lower limit, in a ½-liter flask, gave 2.55 percent for n-propyl alcohol, 2.65 percent for isopropyl alcohol (221); in a 1-inch-diameter closed tube, 2.5 percent for isopropyl alcohol (294).

Influence of Temperature.—The lower limit of propyl alcohol, with downward propagation of flame in a 2½-liter bottle, fell from 2.45 percent at 100° C. to 1.75 at 250° (21, 23). (The constants given in the first reference and the name in the second indicate that the term "butyl alcohol" was used by mistake in the first reference.) In a 2.3-liter bottle, direction of flame unspecified, the limits of isopropyl alcohol were 2.02 and 7.99 percent at 70° C. and 1.73 and 7.35 percent at 130° C. (231).

Influence of Water.—Some experiments suggest that the lower limit of isopropyl alcohol is raised by the addition of water vapor (231).

BUTYL ALCOHOL

The limits of n-butyl alcohol in air, with upward propagation of flame in a closed bomb 4 inches in diameter and 38 inches in length, at a temperature sufficient to vaporize the alcohol, are 1.45 and 11.25 percent (138).

Influence of Temperature.—The lower limit with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39.0 cm. in length, vented at its upper end, is 1.56 percent at 100° C., 1.27 at 200° C., and 1.22 at 225° C. (239).

Older determinations of the lower limit are 1.68 percent isobutyl alcohol in a ½-liter flask (221) and 1.70 percent butyl alcohol under unspecified conditions (101).

AMYL ALCOHOL

The lower limit of amyl alcohol in air is 1.19 percent in a ½-liter flask (221) and 1.20 percent under unspecified conditions (101).

ALLYL ALCOHOL

The limits of allyl alcohol in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top, are 2.50 and (at a sufficient temperature to vaporize the alcohol) 18.0 percent (138).

Older determinations of the lower limit gave 3.04 percent in a ½-liter flask (221) and 2.4 percent under unspecified conditions (101).

FURFURYL ALCOHOL

The limits of furfuryl alcohol in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top, at a temperature sufficient to vaporize the alcohol, are 1.80 and 16.30 percent (138).

PROPYLENE GLYCOL; TRIETHYLENE GLYCOL

The limits of propylene and triethylene glycols in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top, at a temperature sufficient to vaporize the substance, are 2.62 and 12.55 percent, and 0.89 and 9.20 percent, respectively (138).

METHYL ETHER

METHYL ETHER IN AIR

The limits of methyl ether in air, with upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, are 3.45 and 15.1 percent. When the firing end is closed and ignition is caused by a heated platinum spiral instead of a flame, the higher limit becomes 26.7 percent and the propagation is by "cool flame" (171).

In narrow tubes (1 to 2.5 cm. in diameter), the previous history of the tube affected the results; the widest range was 3.93 to 16.6 percent (262).

METHYL ETHER IN OXYGEN

An old observation placed the higher limit of methyl ether in oxygen, with downward propagation of flame in a 2-cm. cube, between 42 and 49 percent methyl ether (243). Recent experiments in tubes of diameters from 1 to 2.5 cm. gave results varying with the previous history of the tube; the widest range was 3.90 and 51.4 percent (262).

METHYL ETHER IN OTHER ATMOSPHERES

Atmospheres of Air and Dichlorodifluoromethane.—The addition of dichlorodifluoromethane to air narrows the range of flammability of methyl ether until, when 17.6 percent or more is present, no mixture is flammable (171).

METHYL ETHYL ETHER

The limits of methyl ethyl ether in air, conditions not specified, are 2.0 and 10.1 percent (101).

ETHYL ETHER

ETHYL ETHER IN AIR

Extraordinarily large differences are to be found between the various figures recorded for the higher limit of ethyl ether in air. These are to be explained by the phenomenon of "cool flames," by which rich mixtures suitably ignited can propagate partial combustion slowly, with a comparatively small rise of temperature but with the normal appearance of a flame, in the upward or horizontal direction. In a 2-inch-diameter horizontal tube the higher limit of the "ordinary" flame merges with the lower limit of the "cool" flame at atmospheric pressure but becomes separate at lower pressures (359). In a 1-inch-diameter tube the ranges for the ordinary and cool flames are separate at atmospheric

pressure (353). (See below under Influence of Pressure.)

Two observations of the limits of ether in air have been made with upward propagation of flame in a 2-inch-diameter tube, open at the firing end. These gave 1.92 and 48.5 percent (31), and 1.85 and 25.9 percent (183); in the latter tests the source of ignition was presumably unfavorable to the initiation of a "cool" flame.

Table 31 summarizes other determinations of the limits of ethyl ether in air.

The limits in a small vessel have been stated to be 1.2 and 51.0 percent (9); and, with an obviously weak spark, 3.14 and 9.5 percent (327). A lower limit of 1.67 has also been reported (302).

The lower limits in a 5-cm. glass tube closed at both ends differed only in the second decima

TABLE 31.—*Summary of other determinations of limits of flammability of ethyl ether in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Far end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length			Lower	Higher		
15	300 (iron)	Closed	Open	1.73	23.30	Dry	361
10.2	66 (iron)	do	Closed	1.95	36.5	do	183
7.5	150 (glass)	do	do	1.71	48	do	353
6.0	120 (glass)		do	2.1		Partly dried	325
5	150 (iron)	Closed	Open	2.24	15.45	do	361
5	150 (glass)	do	do	1.93	15.75	do	361
5	150 (glass)	do	Closed	1.84	48	do	353
5	91 (glass)	do	do	1.95	15.60	do	351
2.5	150 (glass)	do	do	2.00	47	do	353
2.5	25 (glass)	Central ignition	do	1.25	10.0	Undried	294

Horizontal Propagation of Flame

15	300 (iron)	Closed	Open	1.80	22.30	Dry	361
7.5	150 (glass)	do	Closed	1.75	40	do	353
5	150 (iron)	do	Open	2.29	7.95	do	361
5	150 (glass)	do	do	2.05	8	do	361
5	150 (glass)	do	Closed	1.88	33	do	353
5	91 (glass)	do	do	2.05	8	do	351
2.5	150 (glass)	do	do	{ 1.98 14 [1]	6.25 25 [1] }	do	359

Downward Propagation of Flame

15	300 (iron)	Closed	Open	1.93	6.50	Dry	361
7.5	150 (glass)	do	Closed	1.85	6.40	do	353
6.2	33 (glass)	Open	do	1.6		Saturated	95
5	150 (iron)	Closed	Open	2.34	6.70	Dry	361
5	150 (glass)	do	do	2.15	6.15	do	361
5	91 (glass)	do	Closed	2.15	6.15	do	351
5	65 (glass)	do	do	1.89	6.7	do	316
5	65 (glass)	Partly open	Partly open	1.93	6.66	do	256
2.5	150 (glass)	Closed	Closed	1.97	6.15	do	353
1.9	33 (glass)	Open	do	2.75	7.70	Saturated	95

[1] Cool flame range, separate from the ordinary flame range.

place from those obtained when a small stop-cock was opened at one end or the other; the higher limits differed by not more than 1 percent. Similar differences were observed when the length of the tube was varied from 100 to 250 cm. and when the point of ignition was brought forward about 6 cm. (*353*).

Influence of Pressure.—As the pressure is reduced below normal, the range of flammable mixtures in a horizontal tube 5 cm. in diameter divides into two. At 500 mm. pressure the range is 1.88 to 9.25 percent for the ordinary flame and 13 to 33 percent for the cool flame. As the pressure is reduced further, each range is contracted, and a little below 400 mm. the cool flame is no longer propagated. At 90 mm. the range for the ordinary flame has contracted to 2.32 to 6.1 percent (*359*). Similar observations have been made with a tube 2.5 cm. in diameter (*331*).

The effect of reduced pressure on the limits of ignitibility of ethyl ether in air by a standard spark, rather than its limits of flammability, has been examined (*8, 13*).

Increase of pressure above atmospheric widened the range at both ends when the temperature was raised to maintain enough ether vapor for the test. The effect may be due more to the change of temperature than to the change of pressure (*14*).

Influence of Temperature.—The higher limit of ether in air is appreciably increased by a rise of 40° C. (*361*). (*See also* next paragraph.)

Influence of Pressure and Temperature Together.—The limits of ether in air have been observed, with horizontal propagation of flame in a closed tube 2.5 cm. in diameter, at pressures up to 4,000 mm. and temperatures of 20°, 50°, 100°, and 150° C. The limits of both ordinary and cool flames are widened by an increase in temperature; therefore, the two ranges meet at lower pressures as the temperature is raised. A third type of flame, green in color, is observable in certain circumstances (*125, 331, 332*). The relation between cool flames and normal flames is shown in diagrams and discussed, and conditions under which a cool flame may become a normal flame are given (*126*).

The limits in a cylindrical bomb of 700 cc. capacity, after heating under pressure for 30 to 45 minutes to allow preflame combustion to occur, are shown in table 32. The limits are expressed in percentages by weight; the range widens at first with increase of temperature but narrows when preflame combustion becomes evident. The bomb was filled at atmospheric temperature to an initial pressure of 5.8 atmospheres (*245*).

TABLE 32.—*Limits of ethyl ether in air at increased pressures and temperatures*

Temperature, ° C.	Pressure	Limits, percent by weight	
		Lower	Higher
125	Not stated	7.8	32.0
140	.....do.	6.0	32.3
155	.....do.	5.1	32.3
170	.....do.	4.3	32.1
172.5	.....do.	4.0	31.5
175	.....do.	3.7	(1)

[1] Spontaneous inflammation.

Influence of Streaming Movement of Mixture.—The limits were widened several tenths of 1 percent when velocities up to 9 cm. a second were imparted to the mixtures (*361*).

Influence of Impurities.—The presence of diethyl peroxide and of ethyl hydrogen peroxide scarcely affected the lower limit, but any large quantity raised the higher limit (*361*). The lower limit was unaffected by small additions of diethyl selenide or lead tetraethyl. The effect of pyridine (one experiment) accorded with Le Chatelier's formula (*313*).

ETHYL ETHER IN OXYGEN

The lower limit of ethyl ether in oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, is 2.0 percent (*162*); in a closed tube 10.2 cm. in diameter and 96 cm. in length, 2.10 percent. The higher limit with upward propagation in a tube 4.4 cm. in diameter and 60 cm. in length, open at the upper end, is 82.0 percent (*183*).

The limits with downward propagation of flame in a narrow burette are 1.7 and 39.5 percent ether (*205*). The higher limit with downward propagation of flame in a closed tube 4 cm. in diameter is 65 percent; in the presence of 5 percent of carbon dioxide, 60 percent (*124*). The limits in a small vessel, obviously with a weak spark, are given as 2.98 and 45.5 percent (*327*).

ETHYL ETHER IN OTHER ATMOSPHERES

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of ethyl ether in air deficient in oxygen have been determined in a small bulb. As the oxygen was reduced, the lower limit remained nearly constant, but the higher limit fell rapidly; the limits coincided at 10.7 percent oxygen (*13*).

Atmospheres of Oxygen and Helium.—The limits of ethyl ether in all mixtures of oxygen and helium, with upward propagation of flame in a 2-inch-diameter tube open at the lower end, are shown in figure 48 (*162, 163*).
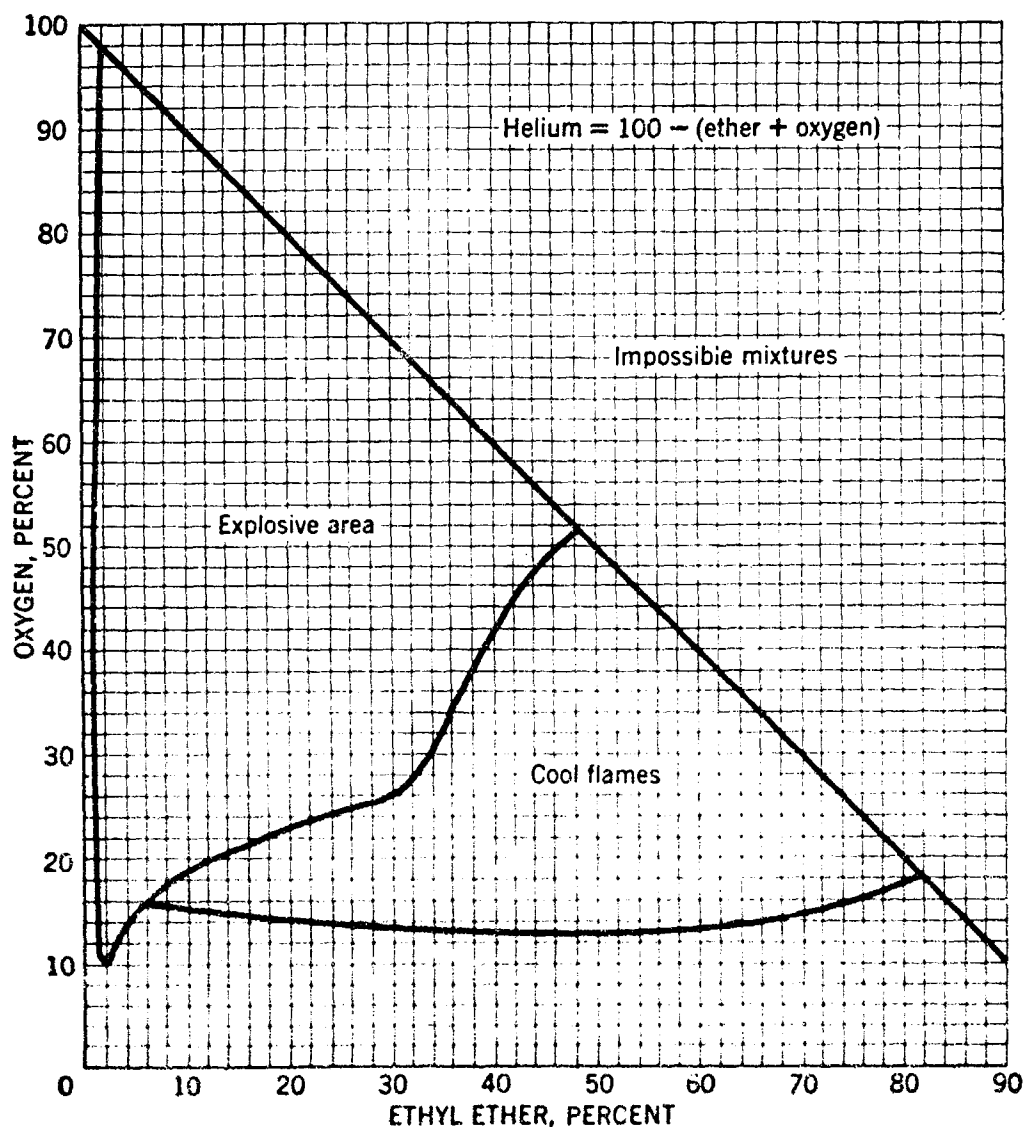
FIGURE 48.—Flammability of Ethyl Ether-Oxygen-Helium Mixtures.

Atmosphere of Nitrous Oxide.—The limits of ethyl ether in nitrous oxide, with upward propagation of flame in a 2-inch-diameter tube, are 1.50 and 24.2 percent (*163*). With downward propagation of flame in a narrow burette they are 3.3 and 25.7 percent ether (*205*); in a vessel 320 cc. in capacity, 1.5 and 16 percent (*60*).

Atmospheres of Air and Nitrous Oxide.—The limits of ethyl ether in a series of mixtures of air and nitrous oxide have been determined for downward propagation of flame in a narrow burette (*205*).

The higher limit, with downward propagation of flame in a closed tube 4 cm. in diameter, is

30 percent ether when oxygen forms 10 percent of the whole mixture (*124*).

Atmospheres of Oxygen and Nitrous Oxide.—The composition of all flammable mixtures of ethyl ether, oxygen, and nitrous oxide, is shown in figure 49. The determinations were made with upward propagation of flame in a 2-inch-diameter tube open at the lower end (*163, 181*). For downward propagation of flame in a narrow burette, *see* reference (*205*).

Atmospheres of Nitrous Oxide and Helium.—The compositions of all flammable mixtures of ethyl ether, nitrous oxide, and helium are shown in figure 50 (*163*).
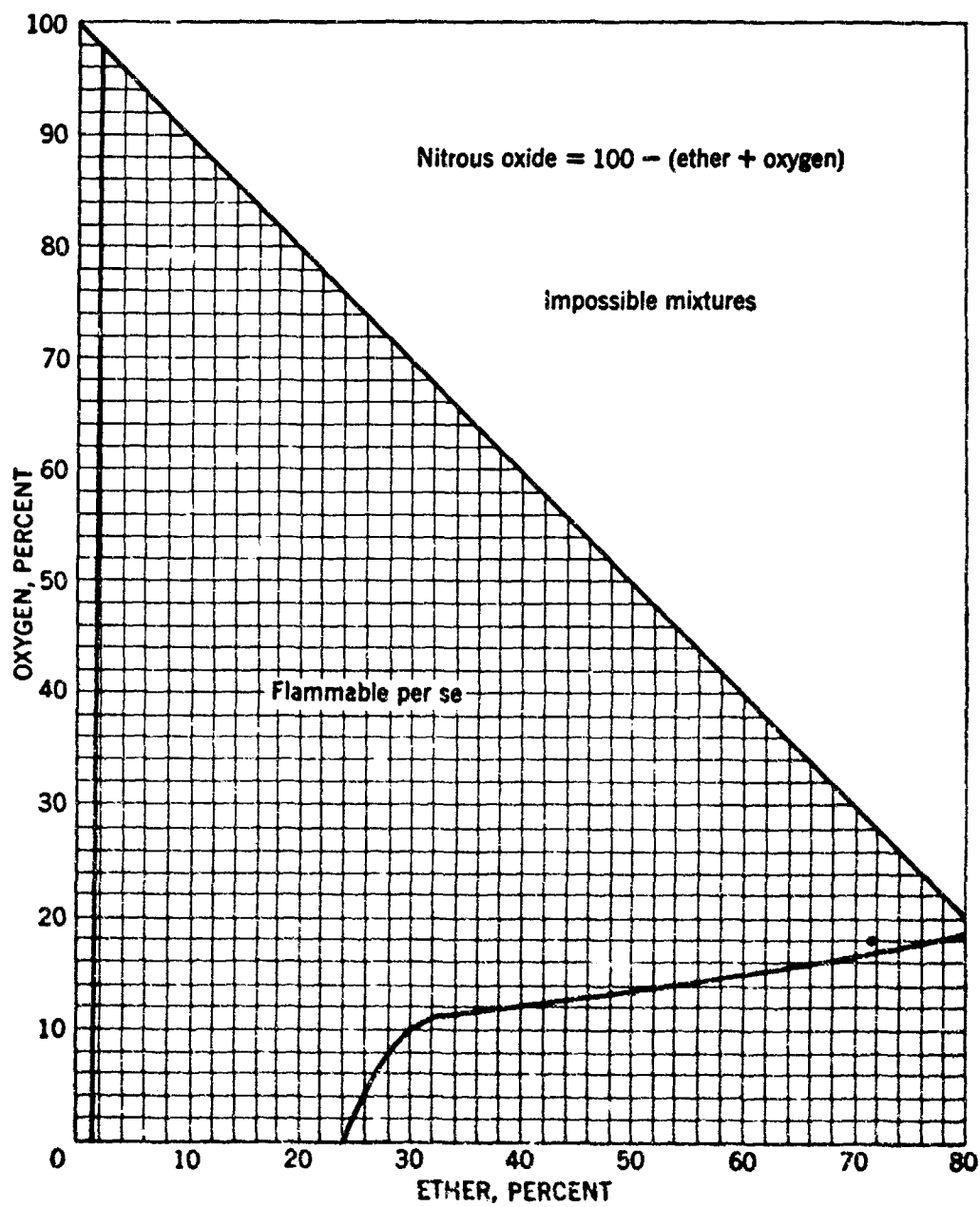
FIGURE 49.—Flammability of Ethyl Ether-Oxygen-Nitrous Oxide Mixtures.
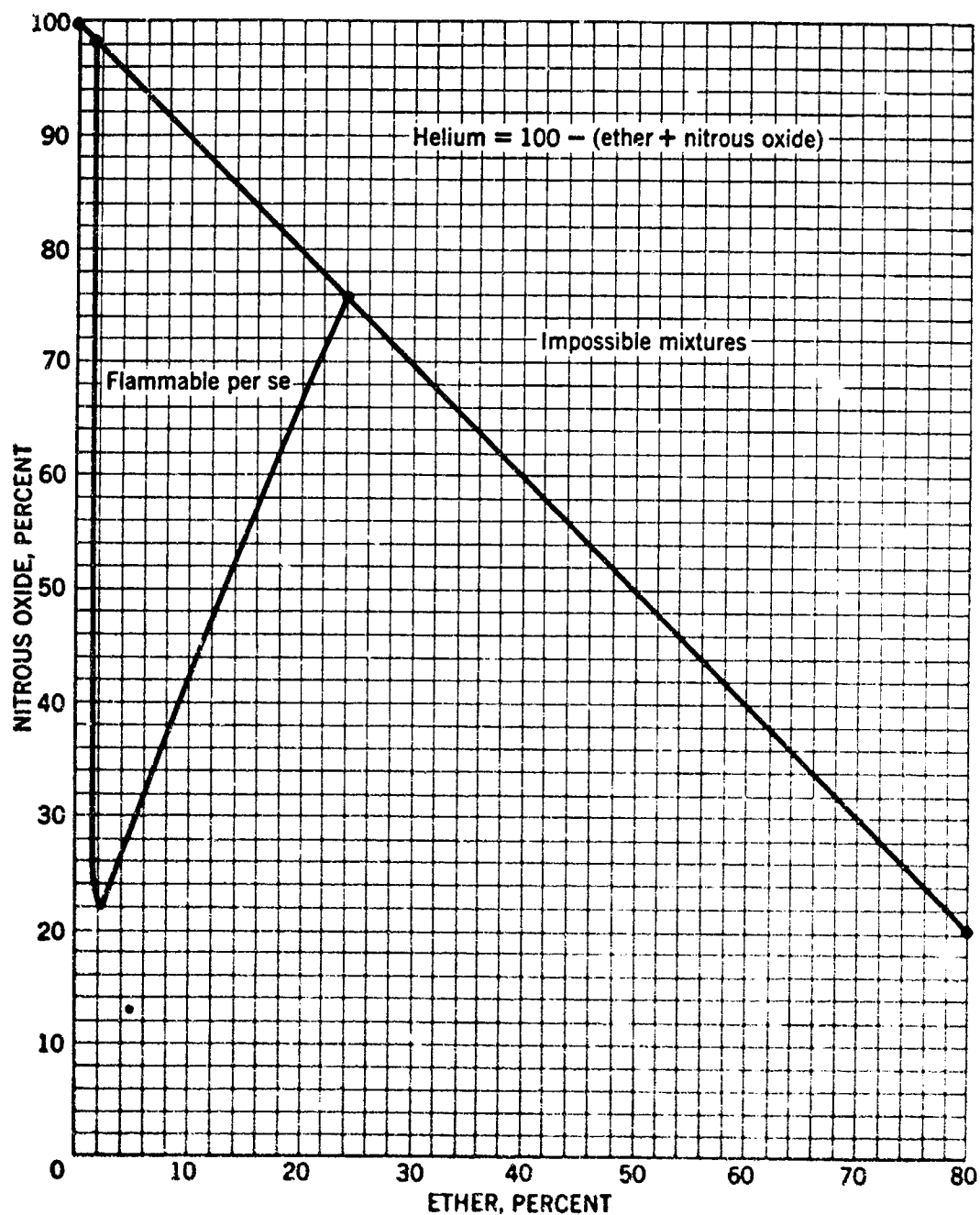
FIGURE 50. -- Flammability of Ethyl Ether-Nitrous Oxide-Helium Mixtures.

ETHYL PROPYL ETHER

The limits of ethyl n-propyl ether in (a) air and (b) oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are (a) 1.9 and 24 percent and (b) 2.0 and 78 percent (234).

PROPYL ETHER

PROPYL ETHER IN AIR

The limits of isopropyl ether in air, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, have been given as 1.38 and 7.90 percent (138) and 2.1

and 21 percent (234). Presumably "cool flames" were obtained in the latter experiments, not in the former.

Another observation, made in a 2.3-liter bottle, direction of propagation unspecified, gave 1.17 and 4.9 percent as the limits of isopropyl ether in air at 100° C. (231).

PROPYL ETHER IN OXYGEN

The limits of isopropyl ether in oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are 2.2 and 69 percent (234).

VINYL ETHER

VINYL ETHER IN AIR

The limits of vinyl ether in air, with upward propagation of flame in a closed tube 10.2 cm. in diameter and 96 cm. in length, are 1.70 and 27.9 percent. The higher limit, with upward propagation in a tube 2 inches in diameter and 6 feet in length, open at the firing end, is 26.5 percent (140).

Effect of Impurity.—The presence of 3.5 percent of ethyl alcohol in vinyl ether is almost without effect on the limits (140).

VINYL ETHER IN OXYGEN

The lower limit of vinyl ether in oxygen, with upward propagation of flame in a closed tube 4 inches in diameter and 38 inches in length, is 1.85 percent. The higher limit, with upward propagation in a tube 1.75 inches in diameter and 23.5 inches in length, open at the top, is 85.5 percent at a temperature sufficient to maintain this proportion of vapor (140).

Effect of Impurity.—The presence of 3.5 percent ethyl alcohol in vinyl ether does not affect the lower limit, but the higher limit is reduced from 85.5 to 80.5 percent (140).

VINYL ETHER IN OTHER ATMOSPHERES

Atmosphere of Nitrous Oxide.—The limits of vinyl ether in nitrous oxide, with upward propagation of flame in a 2-inch tube, open at the lower end, are 1.40 and 24.8 percent (163).

ETHYLENE OXIDE

ETHYLENE OXIDE IN AIR

The limits of ethylene oxide in air, with upward propagation of flame in tubes 5 and 6 cm. in diameter and 150 cm. in length, open at the firing end, are 3.0 and 80 percent (143). The richer mixtures in this range burn at the bottom of the explosion tube, sometimes for 30 seconds, then a very pale blue flame passes slowly to the top of the tube.

In a closed tube, 5 cm. in diameter with hot-wire ignition, all mixtures containing more than 3.6 percent of ethylene oxide propagate flame upward. Above 68 percent the flame is pale blue. At 100 percent a "decomposition flame," still less luminous, is propagated with higher speed (37).

In a 1-liter closed bottle, mixtures containing between 80 and 90 percent of ethylene oxide were inflamed after several seconds sparking (224).

The lower limit in a eudiometer tube 13 mm. in diameter is 3.75 percent for upward propagation of flame and 3.25 for downward propagation (79). Perhaps these figures should be interchanged.

The lower limit in a Hempel pipette 150 cc. in capacity is 4.35 percent. In a flask 6 5 liters in capacity, the limits with downward propagation of flame are 3.3 and 80 percent ethylene oxide (53).

Effect of Pressure.—The effects of reduced pressure on the limits of ethylene oxide in air, with upward propagation of flame in a closed tube 5 cm. in diameter, are shown in figure 51 (37). Neither the blue flame with rich mixtures nor the "decomposition flame" is propagated downward, and the higher limit then corresponds approximately to the broken line in the figure 51.

In a pipette of 50 cc. capacity, the lower limit fell from about 3.7 percent at atmospheric pressure to about 2.8 percent at 550 mm. and then rose to 6.5 percent, where it met the upper limit at a very small pressure (apparently only a few mm. of mercury) (279).

ETHYLENE OXIDE IN OTHER ATMOSPHERES

Atmospheres of Air and Carbon Dioxide.—The limits of ethylene oxide in all mixtures of air and carbon dioxide are shown in figure 52. The determinations were made as described in the first paragraph under Ethylene Oxide in Air. The upper part of the curve applies to the curious type of pale blue flame mentioned (143, 185).

From the data in figure 52 it can be shown that, to render all possible mixtures of ethylene oxide and air nonflammable at ordinary temperatures and pressures, at least 7.15 volumes of carbon dioxide are required per unit volume of ethylene oxide. As the molecular weights of these two substances are equal, 7.15 pounds of carbon dioxide mixed with each pound of ethylene oxide will render it incapable of making a flammable mixture with air (143).

From experiments in a 1-liter closed bottle, it was deduced that at least 10 volumes of carbon dioxide are required, per unit volume of ethylene oxide, to render nonflammable all possible mixtures with air (224).
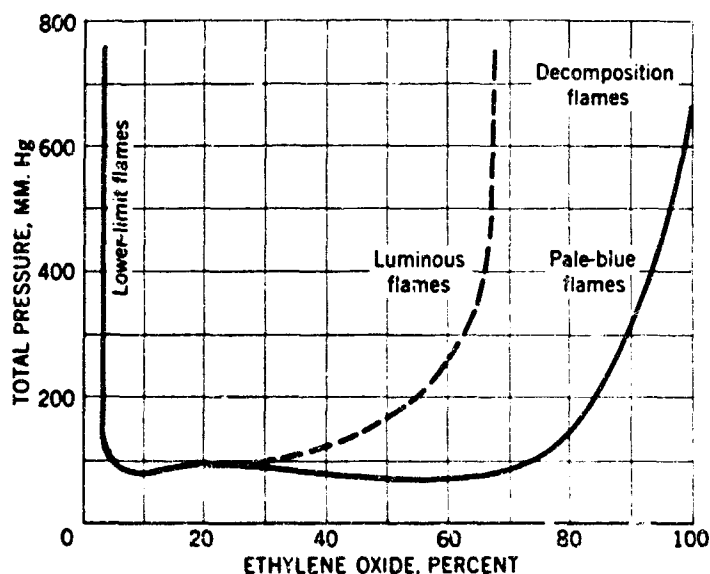
FIGURE 51.—Flammability of Ethylene Oxide-Air Mixtures at Reduced Pressures.
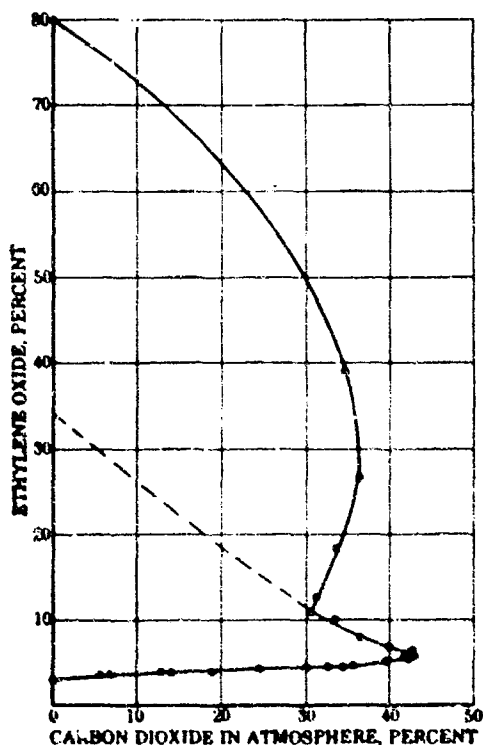
FIGURE 52. Limits of Flammability of Ethylene Oxide in Air and Carbon Dioxide.

Effect of Pressure.—The limits of a series of mixtures of ethylene oxide and carbon dioxide (from 1 : 1 to 1 : 7) at various pressures below atmospheric have been determined in a 50-cc. pipette. The results are graphed (279).

PROPYLENE OXIDE

PROPYLENE OXIDE IN AIR

The limits of propylene oxide in air, with upward propagation of flame in a tube 6 cm. in diameter, open at the firing end, are about 2.1 and 21.5 percent (185).

PROPYLENE OXIDE IN OTHER ATMOSPHERES

Atmospheres of Air and Carbon Dioxide.—One volume of propylene oxide needs 11.0 volumes of carbon dioxide to make a mixture that is nonflammable in air (185).

DIOXANE

The lower limit of dioxane in air, with upward propagation of flame in a closed tube 4 inches in diameter and 38 inches in length, is 1.97 percent. The higher limit, with upward propagation in a tube 2.5 inches in diameter and 36 inches in length, open at the top, is 22.5 percent at 100° C. (179).

TRIOXANE

The limits of trioxane in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top, are 3.57 and 28.70 percent (138).

ACETAL

The lower limit of acetal in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, is 1.58 percent (138). The higher limit, with upward propagation of

flame in a 2-inch-diameter tube, the mixture being at 450 to 500 mm. pressure initially but attaining atmospheric pressure during the propagation of flame, is 10.40 percent (138).

METHYL CELLOSOLVE (GLYCOL MONOMETHYL ETHER)

The lower limit of methyl cellosolve in air, with upward propagation of flame in a tube 2 inches in diameter and 18 inches in length, vented at its upper end, is 2.50 percent at 125° C. Its higher limit is 19.8 percent at 140° C. (138).

ETHYL CELLOSOLVE (GLYCOL MONOETHYL ETHER)

The lower limit of ethyl cellosolve in air, with upward propagation of flame in a tube 2 inches in diameter and 18 inches in length, vented at its upper end, is 1.82 percent at 140° C. Its higher limit is 14.00 percent at 150° C. (138).

BUTYL CELLOSOLVE (GLYCOL MONOBUTYL ETHER)

The lower limit of butyl cellosolve in air, with upward propagation of flame in a tube 2 inches in diameter and 18 inches in length, vented at its upper end, is 1.13 percent at 170° C. Its higher limit is 10.6 percent at 180° C. (138).

DIETHYL PEROXIDE

The lower limit of diethyl peroxide in air, with downward propagation of flame in a 2-inch-diameter tube, is 2.34 percent (361).

ACETALDEHYDE

ACETALDEHYDE IN AIR

The limits of acetaldehyde in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 4.12 and 55.0 percent (138).

Table 33 summarizes other determinations of the limits of flammability of acetaldehyde in air.

ACETALDEHYDE IN OXYGEN

The limits of acetaldehyde in oxygen, conditions not stated but probably in a closed 2-inch-diameter tube, are 4 and 93 percent (129).

ACETALDEHYDE IN OTHER ATMOSPHERES

The limits of acetaldehyde in an atmosphere of 21 percent oxygen, 19 percent nitrogen, and 60 percent carbon dioxide are 8.1 and 11 percent with downward propagation in a 1.7-cm. tube (188).

TABLE 33.—*Summary of other determinations of limits of flammability of acetaldehyde in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
7.5	150	Closed......	3.97	57	Dry........	356
5	150	......do.......	4.21	57		356
			{4.0	17.0	}	352
			[1]17.0	[1]61.5		

Horizontal Propagation of Flame

7.5	150	Closed.....	{4.23	16.7	}Dry........	356
			[1]21	[1]48		
5	150	......do......	{4.32	16	} ....do......	356
			[1]25	[1]45		

Downward Propagation of Flame

7.5	150	Closed......	4.27	13.4	Dry........	356
5	150	.....do.......	4.36	12.8	....do.......	356
1.7	....	.....do.......	5.7	13.5		188

[1] These limits are for the "cool flame."

In an atmosphere of 21 percent oxygen and 79 percent carbon dioxide no mixture with acetaldehyde could propagate flame downward in a 1.7-cm. tube (188).

PARALDEHYDE

The lower limit of paraldehyde in air, conditions not specified, is 1.3 percent (101).

BUTYRALDEHYDE

The lower limit of butyraldehyde in air, with upward propagation of flame in a 2-inch-diameter tube, is 2.47 percent (138).

ACROLEIN

The limits of acrolein in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 2.85 and 30.5 percent (138).

CROTON ALDEHYDE

The limits of croton aldehyde in air, with upward propagation of flame in a closed tube 10.2 cm. in diameter and 96 cm. in length, are 2.12 and 15.5 percent (135).

FURFURAL

The lower limit of furfural in air, with upward propagation of flame in a tube 5 cm. in diameter and 150 cm. in length, open at the firing end, is 2.10 percent at 125° C. (164).

ACETONE

ACETONE IN AIR

The limits of acetone in air, with upward propagation of flame in a tube 5 cm. in diameter, open at the firing end, are 3.0 and 10.80 percent (*138*) or 3.1 and 11.15 percent (*31*).

Table 34 summarizes other determinations of the limits of acetone in air.

The limits in a 2-liter flask and a 13-liter flask, with ignition near the base, are 2.5 and 10.4 percent (*76*). Two older figures for the lower limit, probably for downward propagation of flame, are 2.9 and 2.7 percent (*213*, *221*). The limits in a very small vessel have been stated as 1.6 and 15.3 percent (*9*). The agreement of the figures in table 34 is poor.

Unusual difficulties have arisen in the interpretation of observations of the nature and progress of flame in acetone-air mixtures. Thus, one observer writes (*353*):

The greatest difficulty was found with acetone. * * * The (higher-limit) figures finally taken were the highest values obtained in any of a great number of trials. Below the values given an ignition would often occur and a flame only go halfway up the tube * * * The fact that a flame goes only halfway or less along a tube is no proof that the mixture is above the limit in that tube * * * In a 7.5-cm. tube near the upper limit upward a mixture which only propagated flame 50 cm. or less would often propagate flame much farther at the second trial and at the third all the way to the top.

TABLE 34.—*Summary of other determinations of limits of flammability of acetone in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Far end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length			Lower	Higher		
30. 6	39 (iron)	Closed	Open	2. 67		Undried	*239*
15	300 (iron)	do	do	2. 88	12. 40	Dry	*361*
10. 2	96 (iron)	do	Closed	2. 55	12. 80	do	*142*
10. 2	96 (iron)	do	do	2. 64		85 percent saturated.	*142*
10	75 (glass)	do	do	2. 15	9. 7	Dry	*352*
7. 5	150 (glass)	do	do	2. 89	11. 8	do	*353*
5	150 (iron)	do	Open	3. 80		do	*361*
5	150 (glass)	do	do	2. 89	12. 20	do	*361*
5	150 (glass)	do	Closed	2. 90	12. 6	do	*353*
5	150 (glass)	do	do	2. 20	9. 5	do	*352*
2. 5	150 (glass)	do	do	3. 12	12. 95	do	*353*
2. 5	60 (glass)	do	do	2. 30	7. 5	do	*352*
2. 5	25 (glass)	(Central ignition)	do	2. 5	9. 0	Undried	*294*

Horizontal Propagation of Flame

Diameter	Length	Firing end	Far end	Lower	Higher	Content	Ref.
15	300 (iron)	Closed	Open	2. 89	12. 40	Dry	*361*
10	75 (glass)	do	Closed	2. 20	9. 5	do	*352*
7. 5	150 (glass)	do	do	2. 92	11. 9	do	*353*
5	150 (iron)	do	Open	3. 90		do	*361*
5	150 (glass)	do	do	3. 04	9. 15	do	*361*
5	150 (glass)	do	Closed	2. 96	9. 9	do	*353*
5	150 (glass)	do	do	2. 25	9. 3	do	*352*
2. 5	150 (glass)	do	do	3. 10	8. 25	do	*353*
2. 5	60 (glass)	do	do	2. 40	6. 7	do	*352*

Downward Propagation of Flame

Diameter	Length	Firing end	Far end	Lower	Higher	Content	Ref.
22. 5	33.5 (iron)	Open	Closed	2. 5	[1] 10		*106*
15	300 (iron)	Closed	Open	3. 11	10. 90	Dry	*361*
10	75 (glass)	do	Closed	2. 35	8. 5	do	*352*
7. 5	150 (glass)	do	do	2. 93	8. 6	do	*353*
5	150 (iron)	do	Open	4. 00		do	*361*
5	150 (glass)	do	do	3. 15	8. 35	do	*361*
5	150 (glass)	do	Closed	2. 99	8. 40	do	*353*
5	150 (glass)	do	do	2. 40	8. 3	do	*352*
5	65 (glass)	do	do	3. 00		do	*316*
2. 5	150 (glass)	do	do	3. 15	8. 25	do	*353*
2. 5	60 (glass)	do	do	2. 75	6. 5	do	*352*

[1] Approximately.

Influence of Pressure.—The effect of reduced pressure on the limits of ignitibility of mixtures of acetone and air by a standard spark, rather than their limits of flammability, have been examined (*13*).

Influence of Temperature.—The lower limit of acetone in air, with upward propagation of flame in a tube 2 inches in diameter, is 3.00 at laboratory temperature (*138*) and 2.92 at 125° C. (*164*).

The limits with upward propagation of flame in a closed tube 10.2 cm. in diameter and 96 cm. in length widened from 2.55 and 12.80 percent at room temperature to 2.17 and 13.05 percent at 175° C. (*142*).

In a standard machine for coating wire with cellulose acetate, the lower limit with downward propagation of flame fell from 3.0 percent at 65° C. to 2.8 at 150° C.; with middle ignition, horizontal and upward propagation, from 2.9 at 65° to 2.5 at 150° C.; and with propagation against a current produced by a fan, from 3.5 at 65° to 3.0 at 150° C. (*142*).

The lower limit with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39 cm. in length, mixtures undried, vented at its upper end, are 2.67 percent at 21° C., 2.40 at 100° C., and 2.00 at 200° C. (*239*).

The limits with downward propagation of flame in a 2½-liter bottle widened from 2.78 and 8.70 percent at 100° C. to 2.33 and 9.75 percent at 250° C. (*21*, *23*).

ACETONE IN OTHER ATMOSPHERES

For atmospheres of nitrogen and oxygen, carbon dioxide and oxygen, and equal volumes of nitrogen and carbon dioxide mixed with 20.9 percent or less of oxygen, the limits of acetone have been determined in a 2-liter flask with ignition near the base. Curves are given in the original paper (*76*) for the whole region of explosibility. It appears that, when the oxygen content of a nitrogen-oxygen atmosphere is reduced below 13.5 percent, no mixture with acetone will propagate flame (*76*).

Mixtures of acetone and sulfur dioxide, evaporated into the air, can form flammable mixtures only when the ratio of sulfur dioxide to acetone is less than 1.9 by volume (liquid) (*308*).

METHYL ETHYL KETONE

Table 35 gives the observed limits of flammability of methyl ethyl ketone in air.

The lower-limit figures in this table are moderately consistent. In a large space, at atmospheric pressure, the lower limit is probably about 2 percent and the higher not greater than 12 percent.

TABLE 35.—*Limits of flammability of methyl ethyl ketone in air*

Upward Propagation of Flame

Dimensions of tube, cm.		Firing end	Limits, percent		Content of aqueous vapor	Reference No.
Diameter	Length		Lower	Higher		
30. 6	39	Closed (top vented)	1. 83		Undried	*239*
10. 2	96	Closed	1. 83	9. 5	Dry	*150*
7. 5	150	do	1. 97	10. 0	do	*353*
5. 0	150	do	2. 05	9. 9	do	*353*
5. 0	91	do	2. 15	11. 5	do	*351*
2. 5	150	do	2. 12	10. 1	do	*353*

Horizontal Propagation of Flame

Diameter	Length	Firing end	Lower	Higher	Content of aqueous vapor	Reference No.
7. 5	150	Closed	1. 97	10. 2	Dry	*353*
5. 0	150	do	2. 05	8. 5	do	*353*
5. 0	91	do	2. 25	10. 5	do	*351*
2. 5	150	do	2. 12	6. 6	do	*353*

Downward Propagation of Flame

Diameter	Length	Firing end	Lower	Higher	Content of aqueous vapor	Reference No.
7. 5	150	Closed	2. 05	7. 6	Dry	*353*
5. 0	150	do	2. 10	7. 4	do	*353*
5. 0	91	do	2. 40	5. 8	do	*351*
2. 5	150	do	2. 17	6. 3	do	*353*

Influence of Temperature.—The following limits were obtained for upward propagation of flame in a tube 3 inches in diameter, with a loosely fitting cap at the top (*238*):

Initial tempera- ture, ° C.	Lower limit, percent	Higher limit, percent
20	1.8	9.7
100	1.7	9.7
150	1.5	9.8
200	1.3	9.9

The lower limit with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39 cm. in length, vented at its upper end, is 1.83 percent at 21° C., 1.70 at 100° C., and 1.33 at 200° C. (*239*).

METHYL PROPYL KETONE; METHYL BUTYL KETONE

The limits of methyl propyl ketone and methyl butyl ketone in air, with upward propagation of flame in a closed tube 4 inches in diameter and 38 inches in length, are 1.55 and 8.15 percent and 1.35 and 8.0 percent, respectively (*138*).

The limits of methyl isobutyl ketone in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top and at a sufficient temperature to vaporize the substance, are 1.40 and 7.50 percent (*138*).

CYCLOHEXANONE

The lower limit of cyclohexanone in air with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39.0 cm. in length, vented at its upper end, is 1.11 percent at 100° C., 0.96 at 200° C., 0.94 at 225° C., and 0.91 at 250° C. (*239*).

ISOPHORONE

The limits of isophorone in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top and at a sufficient temperature to vaporize the isophorone, are 0.84 and 3.80 percent (*138*).

ACETIC ACID

The lower limit of acetic acid in air, with upward propagation of flame in a closed bomb 4 inches in diameter and 38 inches in length, at a sufficient temperature to vaporize the acid, is 5.40 percent (*138*). An old determination gave the lower limit in air in a 500-cc. flask, apparently with downward propagation of flame, as 4.05 percent at 36° C. (*221*).

ACETIC ANHYDRIDE

The limits of acetic anhydride in air, with upward propagation of flame in a 1-inch-diameter tube, open at the upper end, are: Lower, 2.67 percent (at 47.3° C.); higher, 10.13 percent (at 74.4° C.) (*172*).

PHTHALIC ANHYDRIDE

The limits of phthalic anhydride in air, with upward propagation of flame in a tube 1 inch in diameter, open at its upper end, are: Lower, 1.7 percent (at 140° C.); higher, 10.5 percent (at 193° C.) (*184*).

METHYL FORMATE

METHYL FORMATE IN AIR

The limits of methyl formate in air, with upward propagation of flame in a tube 6 cm. in diameter, open at the firing end, are 5.9 and 20.4 percent (*31*). Slightly narrower limits have been found in similar circumstances (*185*).

In a closed tube 4 inches in diameter and 38 inches in length, the limits with upward propagation of flame are 5.05 and 22.7 percent (*165*).

The lower limit in a closed tube 2½ inches in diameter and 4 feet in length, is 4.4 percent with upward propagation of flame and 4.5 percent with horizontal propagation (*256*).

METHYL FORMATE IN OTHER ATMOSPHERES

Atmospheres of Air and Carbon Dioxide.—One volume of methyl formate needs 2.3 volumes of carbon dioxide to make a mixture that is nonflammable in air (*185*).

ETHYL FORMATE

ETHYL FORMATE IN AIR

The limits of ethyl formate in air, with upward propagation of flame in a tube 6 cm. in diameter, open at the firing end, are about 2.7 and 13.5 percent (*185*).

Other determinations, made in a closed tube 2 inches in diameter and 36 inches in length, are: With upward propagation, 3.5 and 16.4 percent; horizontal, 3.7 and 14.6 percent; and downward, 3.9 and 11.8 percent (*351*).

The limits with upward propagation in a closed iron tube 4 inches in diameter and 38 inches in length are 2.75 and 16.40 percent (*138*).

ETHYL FORMATE IN OTHER ATMOSPHERES

Atmospheres of Air and Carbon Dioxide.—One volume of ethyl formate requires 6.0 volumes of carbon dioxide to make a mixture that is nonflammable in air (*185*).

BUTYL FORMATE

The limits of *n*-butyl formate in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top, are 1.73 and 8.15 percent (*138*).

METHYL ACETATE

The limits of methyl acetate in air, in a closed iron tube 4 inches in diameter and 38 inches in length, with upward propagation of flame, are 3.15 and 15.6 percent (*138*). In a closed tube 2 inches in diameter and 36 inches in length the limits are: With upward propagation of flame,

4.1 and 13.9 percent; horizontal, 4.25 and 11.9 percent; and downward, 4.4 and 10.1 percent (*351*).

ETHYL ACETATE

ETHYL ACETATE IN AIR

The lower limit of ethyl acetate in air, with upward propagation of flame in a tube 6 cm. in diameter, open at the firing end, is 2.55 percent (*31*) and between 2 and 2.5 percent (*185*). The higher limit is between 8 and 9 percent under the same conditions (*185*).

Table 36 summarizes other determinations of the limits of ethyl acetate in air.

TABLE 36.—*Summary of other determinations of limits of flammability of ethyl acetate in air*

Dimensions of tube, cm.		Tube	Limits for propagation, percent						Reference No.
			Upward		Horizontal		Downward		
Diameter	Length		Lower	Higher	Lower	Higher	Lower	Higher	
10. 2	96	Closed	2. 18						*139*
7. 5	150	do	2. 26		2. 29		2. 33		*353*
5. 0	150	do	2. 32	[1] 11. 40	2. 35	[1] 9. 80	2. 37	[1] 7. 10	*353*
2. 5	150	do	2. 44		2. 44		2. 50		*353*
2. 5	25	do	2. 25	11. 0					*294*

[1] At 60° C.

According to old experiments the lower limit in a 2-liter bottle, probably with downward propagation of flame, is 2.3 percent (*221*).

Influence of Temperature.—The lower limit of ethyl acetate in air, with upward propagation of flame in a tube 10.2 cm. in diameter and 96 cm. in length, fell from 2.18 percent at 23° C. to 1.75 percent at 200° C. (*139*).

ETHYL ACETATE IN OTHER ATMOSPHERES

Atmospheres of Air and Carbon Dioxide.— One volume of ethyl acetate requires 6.3 volumes of carbon dioxide to make a mixture that is nonflammable in air (*185*).

VINYL ACETATE

The limits of vinyl acetate in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 2.65 and 13.35 percent (*138*).

PROPYL ACETATE

The limits of propyl acetate in air, with upward propagation of flame in a closed iron tube 4 inches in diameter and 38 inches in length, are 1.77 and (at 90° C.) 8.0 percent

(*138*); another value for the lower limit, with upward propagation of flame in a tube 6 cm. in diameter, open at the firing end, is 2.05 percent (*31*).

ISOPROPYL ACETATE

The limits of isopropyl acetate in air, with upward propagation of flame in a closed iron tube 4 inches in diameter and 38 inches in length, are 1.78 and (at 90° C.) 7.8 percent (*138*); the lower limit with upward propagation of flame in a closed tube 2.5 cm. in diameter and 25 cm. in length, with central ignition, is 2.0 percent (*294*).

BUTYL ACETATE

The lower limit of butyl acetate in air, with upward propagation of flame in a tube 6 cm. in diameter, open at the firing end, is 1.7 percent at 30° C. (*31*).

The limits of *n*-butyl acetate in air, with upward propagation of flame in a closed bomb 4 inches in diameter and 38 inches in length, at a temperature sufficient to vaporize the butyl acetate, are 1.39 and 7.55 percent (*138*).

AMYL ACETATE

The lower limit of amyl acetate in air, with upward propagation of flame in a closed bomb, 4 inches in diameter and 38 inches in length, is 1.10 percent (138); in conditions not stated, 1.1 percent (101).

Influence of Temperature.—The limits of iso-amyl acetate in air, with upward propagation of flame in a glass tube 2 inches in diameter and 18 inches in length, open at the upper end, at 100° C., are 1.22 and 7.45 percent (138). The lower limit, with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39 cm. in length, vented at the top, is 1.00 percent at 100° C., 0.82 at 200° C., and 0.76 at 250° C. (239).

METHYL CELLOSOLVE ACETATE (ACETATE OF GLYCOL MONOMETHYL ETHER)

The lower limit of methyl cellosolve acetate in air, with upward propagation of flame in a tube 2 inches in diameter and 18 inches in length, vented at its upper end, is 1.75 percent at 150° C. Its higher limit is 8.2 percent at 150° C. (138).

METHYL PROPIONATE; ETHYL PROPIONATE

The lower limits of methyl propionate and ethyl propionate in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 2.45 and 1.85 percent, respectively. The higher limits in a similar tube, the mixture being at 450 to 500 mm. pressure

initially but attaining atmospheric pressure during propagation of the flame, are 12.60 and 11.05 percent, respectively (138).

METHYL LACTATE

The lower limit of methyl lactate in air, with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39 cm. in length, vented at its upper end, is 2.21 percent at 100° C., 1.86 at 200° C., 1.80 at 225° C., and 1.75 at 250° C. (239).

ETHYL LACTATE

The lower limit of ethyl lactate in air, with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39 cm. in length, vented at its upper end, is 1.55 percent at 100° C., 1.29 at 200° C., and 1.22 at 250° C. (239).

ETHYL NITRATE

The lower limit of ethyl nitrate in air, with upward propagation of flame in a 5.3-cm.-diameter tube, open at the lower end, is 4.00 percent (93). In a 2-liter bottle, apparently with downward propagation of flame, it is 3.8 percent (221).

ETHYL NITRITE

The lower limit of ethyl nitrite in air, with upward propagation of flame in a 5.3-cm.-diameter tube, open at the lower end, is 4.11 percent (93).

The limits in closed tubes 150 cm. in length are given in table 37.

TABLE 37.—*Limits of flammability of ethyl nitrate in air*

Tube diameter, cm.	Limits for propagation, percent					
	Upward		Horizontal		Downward	
	Lower	Higher	Lower	Higher	Lower	Higher
7.5	3.01		3.51		3.83	15.1
5.0	3.51	>50	3.63	>45	3.91	14.4

In all probability the higher limit with upward propagation of flame is much more than the figure given. White (353) says:

That this compound is capable of transmitting two different flames through the same mixture was shown during an attempted downward ignition in a 5-cm. tube at the upper limit. This mixture, which would have burned downward violently in normal circumstances, on sparking gave a pale-blue flame which moved gently

upward through the 15 cm. between the electrodes and the top of the tube.

CRESOL

The lower limit of m-p-cresol with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39.0 cm. in length, vented at its upper end, is 1.06 percent at 150° C., 0.93 at 200° C., and 0.88 at 250° C.

AMINES AND IMINES

The limits of several amines and one imine, with upward propagation of flame in a 2-inch-diameter tube, are given in table 38. The limits marked with an asterisk were obtained by igniting at 450 to 500 mm. pressure, the pressure rising to atmospheric but not exceeding it as the flame rose. The other limits were obtained with the lower end of the tube open (138).

TABLE 38.—*Limits of flammability of amines and an imine, percent*

	Lower limit	Higher limit
Methyl amine	*4.95	*20.75
Dimethyl amine	*2.80	*14.40
Trimethyl amine	*2.09	*11.60
Ethyl amine	*3.55	*13.95
Diethyl amine	1.77	10.10
Triethyl amine	*1.25	
Propyl amine	*2.01	*10.35
n-Butyl amine	*1.70	*9.75
Allyl amine	2.35 (*2.20)	*22.05
Ethylene imine	*3.60	*45.60

*See text for explanation.

The higher limit of triethyl amine in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top and at a sufficient temperature to vaporize the amine, is 7.90 percent (138).

ACRYLONITRILE

The lower limit of acrylonitrile in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, is 3.05 percent. The higher limit, with upward propagation in a 1-inch-diameter tube, open at the upper end, at 29.4° C., is 17 percent (156).

PYRIDINE

The limits of dry pyridine in air in a closed tube 5 cm. in diameter and 150 cm. in length are as follows (253): Upward propagation of flame, 1.81 and 12.4 percent; horizontal, 1.84 and 9.8 percent; downward, 1.88 and 7.2 percent. The lower limits were determined at 60° C. and the higher limits at 70° C.

NICOTINE

The limits of nicotine in air, with upward propagation of flame in a 1-inch-diameter tube, open at the upper end, are: Lower, 0.75 percent (at 100.5° C.); higher, 4.00 percent (at 139.5° C.) (178).

METHYL CHLORIDE

METHYL CHLORIDE IN AIR

The limits of methyl chloride in air, with upward propagation of flame in a glass tube 2

inches in diameter and 6 feet in length, open at the firing end, are 10.75 and 17.40 percent (ignition by a flame). The limits are wider when an induction-coil spark is used in a 2½-liter bell jar—8.25 and 18.70 percent (132). The widest range was obtained by the use of a 15,000-volt transformer spark in a 7.5-liter cylinder—7.6 and 19.1 percent with upward propagation of flame (362).

The limits, apparently in a 10-liter vessel, of ignition by flame or spark or white-hot wire, are 10 and 15 percent (298); in a spherical bomb (size not stated), spark ignition, 8.9 and 15.5 percent (92); in a cylindrical bomb of 1.2 liters capacity, 8.1 and 17.1 percent (256); in a 7.5-liter cylinder, flame ignition, 8.0 and 18.9 percent (362); in a 1.6-cm.-diameter tube with downward propagation of flame, 9.7 and 14.1 percent (340); and in a Hempel pipette, 8.6 and 18.4 percent (291).

METHYL CHLORIDE IN OXYGEN

The limits of methyl chloride in oxygen, with downward propagation of flame in a tube 3 cm. in diameter, at 600 mm. pressure, are 8.2 and 65.8 percent (89).

METHYL CHLORIDE IN OTHER ATMOSPHERES

Atmospheres of Air and Methyl Bromide.—In a Hempel pipette, 1.3 percent of methyl bromide was sufficient to render all mixtures of methyl chloride and air nonflammable (291).

Atmosphere of Nitrous Oxide.—The lower limit of methyl chloride in nitrous oxide, with downward propagation of flame in a tube 3 cm. in diameter, at 600 mm. pressure, is 5.0 percent (89).

Atmospheres of Air and Dichlorodifluoromethane.—In a 7.5-liter cylinder, mixtures of methyl chloride and air are nonflammable if they contain 10 percent by volume, or more, of dichlorodifluoromethane (362); in a 1.6-cm. tube, 7 percent or more (340). Mixtures containing 35 percent by weight, or less, of methyl chloride in dichlorodifluoromethane are nonflammable when mixed with air in any proportions (362).

METHYL BROMIDE

METHYL BROMIDE IN AIR

All mixtures of methyl bromide and air appear to be incapable of ignition and propagation of flame in a Hempel pipette (291) or in a tube 2 inches in diameter (132), but mixtures containing 13.5 to 14.5 percent were inflamed by an induction-coil spark in a 2½-liter bell jar (132).

METHYL BROMIDE IN OXYGEN

The limits of methyl bromide in oxygen, with upward propagation of flame in a 2-inch-diame-

ter tube, open at its lower end, are 14 and 19 percent (*234*).

METHYLENE CHLORIDE

METHYLENE CHLORIDE IN AIR

Mixtures of methylene chloride and air were not inflamed in a bomb of 1,200 cc. capacity, but in a box 2 feet wide, 2 feet high, and 5 feet 8 inches long, weak flame propagation was reporte l in some tests (*256*). In an open tube 2 inches in diameter and 6 feet in length, with upward propagation of flame and ignition either by spark or by alcohol flame, no mixture of methylene chloride and air would propagate flame (*157*).

METHYLENE CHLORIDE IN OXYGEN

The lower limit of methylene chloride in oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, is 15.5 percent. The higher limit, with upward propagation in a 1-inch-diameter tube, open at the upper end, at 29.1° C., is 66.4 percent (*157*).

METHYLENE CHLORIDE IN OTHER ATMOSPHERES

Atmospheres of Composition Between Air and Pure Oxygen.—Oxygen-air mixtures containing upward of about 25 percent of oxygen can form flammable mixtures with methylene chloride. Data showing the composition of all flammable mixtures, obtained as stated in the previous paragraph but with suitable temperatures to control the amount of vapor for the higher-limit experiments, are reproduced in figure 53 (*157*).

CHLOROFORM

No mixture of chloroform and oxygen or nitrous oxide, or of all three together, is capable of propagating flame downward in a small burette (*205*).

DICHLORODIFLUOROMETHANE AND TRICHLOROFLUOROMETHANE

These substances formed no flammable mixtures with air, even at 100° C. (*256*).
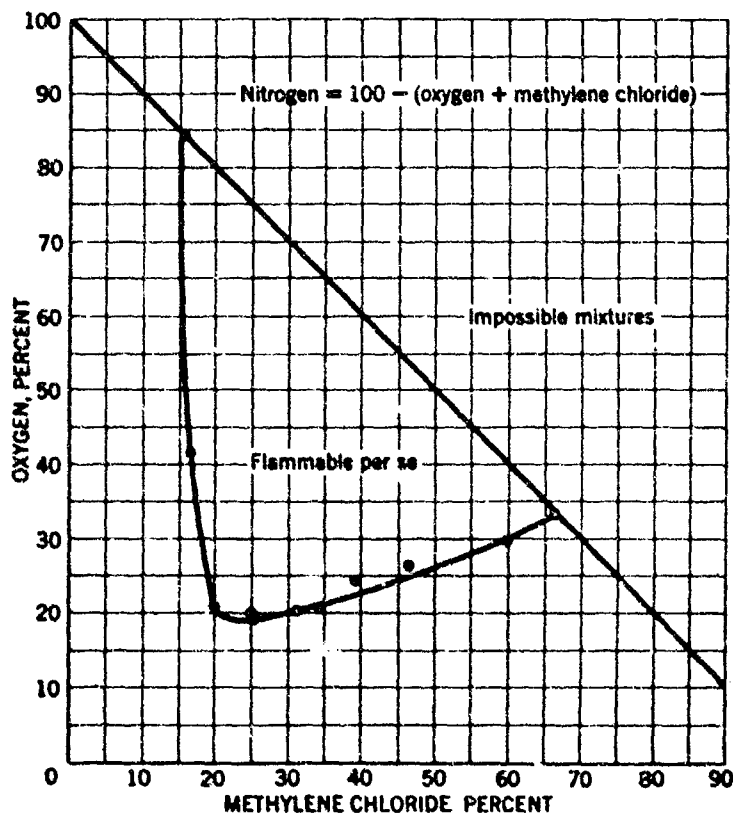
FIGURE 53.—Flammability of Methylene Chloride-Oxygen-Nitrogen Mixtures.

ETHYL CHLORIDE

ETHYL CHLORIDE IN AIR

The limits of ethyl chloride in air, with upward propagation of flame in a glass tube 2 inches in diameter, open at the firing end, were 4.25 and 14.35 percent (ignition by flame) and 3.85 and 15.40 percent (ignition by spark) (*132, 138*). When an induction-coil spark was used in a 2½-liter bell jar the limits were 4.00 and 14.80 percent (*132*). The lower limit with downward propagation in a tube 2 inches in diameter and 2 feet in length, both ends being partly open during inflammation, is 3.95 percent (*246*).

The limits in an explosion pipette, with spark ignition, were 3.6 and 11.2 percent. In a eudiometer tube, with flame ignition, the limits were 6.4 and 11.2 percent. The direction of propagation of flame in these experiments is not stated (*80*).

The limits in a cylindrical bomb of 1.2 liters capacity are 3.7 and 12.0 percent (*256*); in another of 7 liters capacity, with central ignition, they were a little below 5 percent and somewhat above 15 percent (*60*).

ETHYL CHLORIDE IN OXYGEN

The limits of ethyl chloride in oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 4.0 and 62 percent (*234*) and 4.05 and 67.2 percent (*163*).

ETHYL CHLORIDE IN OTHER ATMOSPHERES

Atmosphere of Nitrous Oxide.—The limits of ethyl chloride in nitrous oxide, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 2.10 and 32.8 percent (*163*).

Atmospheres of Air and Dichlorodifluoromethane.—The limits with downward propagation of flame in a 1.6-cm.-diameter tube are given in a diagram (*340*).

ETHYL BROMIDE

ETHYL BROMIDE IN AIR

All mixtures of ethyl bromide and air appear to be incapable of ignition and propagation of flame in a tube 2 inches in diameter, but mixtures containing between 6.75 and 11.25 percent ethyl bromide were inflamed by an induction-coil spark in a 2½-liter bell jar (*132*). In a bomb of 1.2-liter capacity the lower limit is 6.0 percent (*256*).

ETHYL BROMIDE IN OXYGEN

The limits of ethyl bromide in oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are 6.7 and 44 percent (*234*).

ETHYLENE DICHLORIDE

ETHYLENE DICHLORIDE IN AIR

The lower limit of ethylene dichloride in air, with upward propagation of flame in a tube 2 inches in diameter and 4 feet in length, open at the firing end, is 6.2 percent at room temperature and 5.8 at 100° C. The higher limit is 15.9 percent at 100° C. (*145*).

The limits with horizontal propagation of flame in a closed tube 4.5 cm. in diameter and 75 cm. in length are 6.2 and 16.0 percent (*284*), and, with downward propagation of flame in a tube 1.6 cm. in diameter and 30 cm. in length, 6.7 and 12.4 percent (*217*).

ETHYLENE DICHLORIDE IN OTHER ATMOSPHERES

Atmospheres of Air and Carbon Dioxide.—The limits of ethylene dichloride in mixtures of air and carbon dioxide, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, at 100° C., are shown in figure 54. Ethylene dichloride cannot form a flammable mixture with air at 100° C. if 2.3 or more volumes of carbon dioxide are present per unit volume of the dichloride or 1.02 pounds of carbon dioxide per pound of the dichloride (*145*).

Atmospheres of Air and Carbon Tetrachloride.—In a horizontal tube 4.5 cm. in diameter and 75 cm. in length, ethylene dichloride is incapable of forming a mixture flammable with air if more than about 4.5 percent of carbon tetrachloride is present (*284*).

DICHLOROTETRAFLUOROETHANE

This substance was nonflammable when mixed in any proportions with air, even at 100° C. (*256*).

VINYL CHLORIDE

VINYL CHLORIDE IN AIR

The limits of vinyl chloride in air, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are 4.0 and 21.7 percent (*166*).

VINYL CHLORIDE IN OXYGEN

The limits of vinyl chloride in oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are 4.0 and 70 percent (*234*).

DICHLOROETHYLENE (ACETYLENE DICHLORIDE)

DICHLOROETHYLENE IN AIR

The limits of dichloroethylene in air, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are 9.7
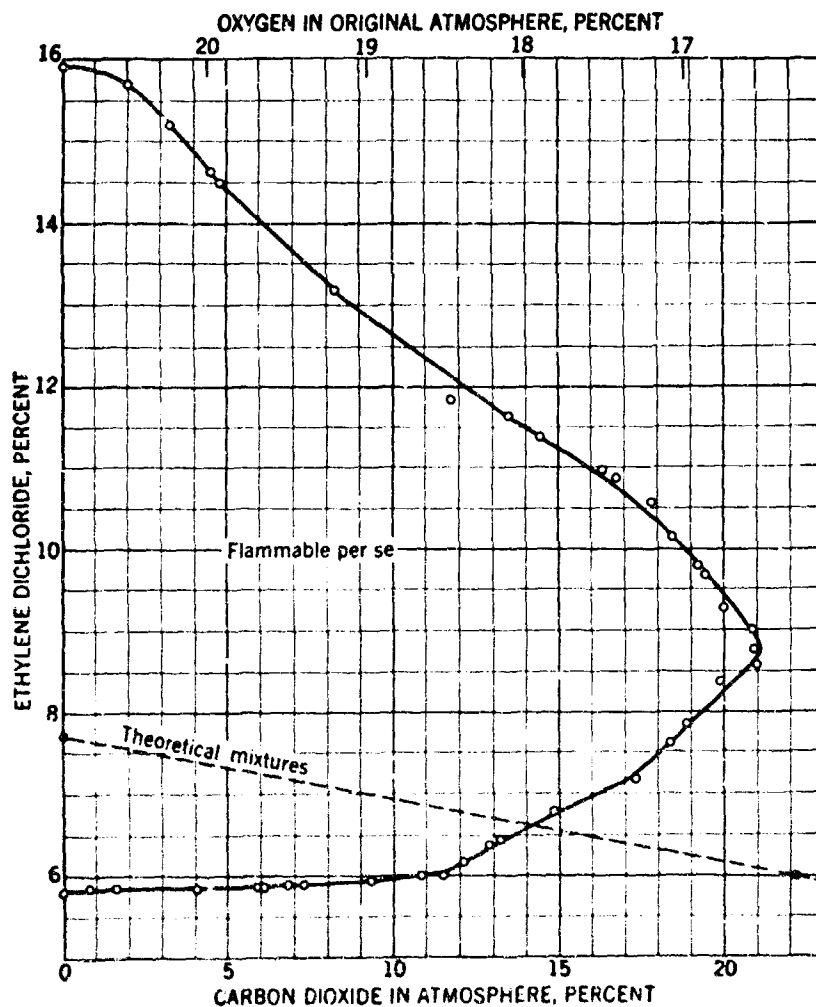
Figure 54.—Limits of Flammability of Ethylene Dichloride in Air and Carbon Dioxide.

and 12.8 percent (71). In a closed tube 2¼ inches in diameter they are given as 5.6 and 11.4 percent (256).

DICHLOROETHYLENE IN OXYGEN

The limits of dichloroethylene in oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are 10 and 26 percent (284).

TRICHLOROETHYLENE

TRICHLOROETHYLENE IN AIR

Trichloroethylene vapor does not form flammable mixtures with air at ordinary temperatures and pressures (173).

TRICHLOROETHYLENE IN OXYGEN

The limits of trichloroethylene in oxygen, with upward propagation of flame in a 1-inch-

diameter tube open at the upper end, are: Lower 10.3 percent (at 25.5° C.); higher, 64.5 percent (at 72° C.) (173).

TRICHLOROETHYLENE IN OTHER ATMOSPHERES

Atmospheres of Composition Between Air and Pure Oxygen.—Oxygen-air mixtures containing upward of 33 percent of oxygen can form flammable mixtures with the vapor of trichloroethylene. The liquid must, however, be suitably warmed, for below 25.5° C. its vapor pressure is too low to enable it to form flammable mixtures (at atmospheric pressure) with oxygen or with any mixture of air and oxygen. Data showing the composition of all flammable mixtures, obtained as stated in the previous paragraph, are reproduced in figure 55 (173).
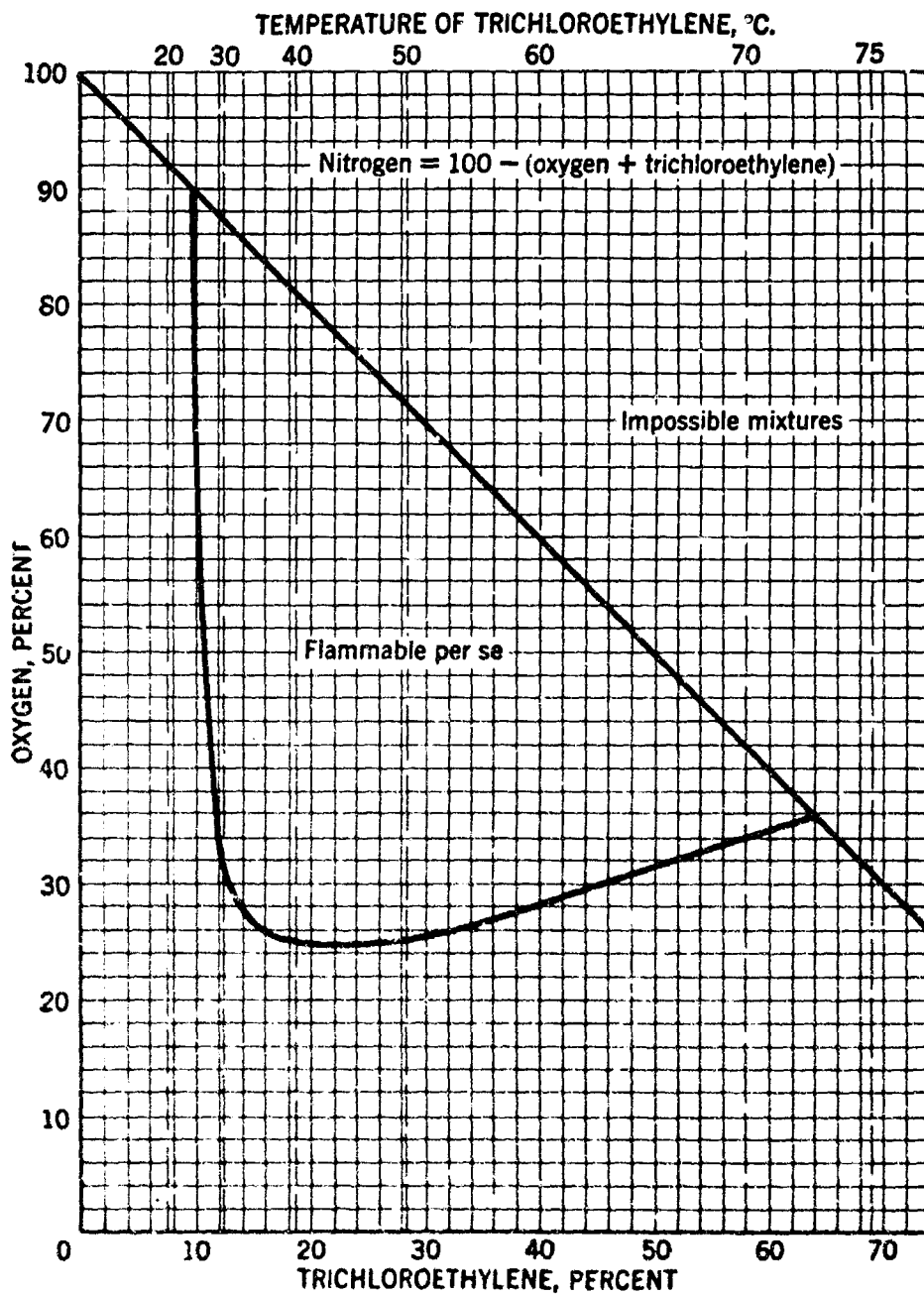
Figure 55.   Flammability of Trichloroethylene, Oxygen, and Nitrogen Mixtures.

ETHYLENECHLOROHYDRIN

The limits of ethylenechlorohydrin in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top, at a temperature sufficient to vaporize the substance, are 4.84 and 15.90 percent (138).

PROPYL CHLORIDE

The limits of n-propyl chloride in air, with upward propagation of flame in a closed bomb, 4 inches in diameter and 38 inches in length, at a temperature sufficient to vaporize the propyl chloride, are 2.60 and 11.10 percent (138).

PROPYL BROMIDE

No mixture of propyl bromide and air could propagate flame downward in a burette 16 to 17 mm. in diameter (190).

PROPYLENE DICHLORIDE

The lower limit of propylene dichloride in air, with upward propagation of flame in a closed tube 4 inches in diameter and 38 inches in length, is 3.4 percent. The higher limit, with upward propagation in a tube 2.5 inches in diameter and 36 inches in length, open at the top, is 14.5 percent at 100° C. (166).

ALLYL CHLORIDE; ALLYL BROMIDE

The limits of allyl chloride and allyl bromide in air, with upward propagation of flame in a 2-inch-diameter tube, open at the firing end, are 3.28 and 11.15 percent, and 4.36 and 7.25 percent, respectively (138).

2-CHLOROPROPENE

The limits of 2-chloropropene (a) in air and (b) in oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are (a) 4.5 and 16.0 percent and (b) 4.5 and 54 percent (237).

BUTYL CHLORIDE

The limits of normal and isobutyl chlorides in air, with upward propagation of flame in a closed bomb 4 inches in diameter and 38 inches in length, at temperatures sufficient to vaporize the chlorides, are 1.85 and 10.10 percent and 2.05 and 8.75 percent, respectively (138).

The limits of isobutyl chloride in air, with downward propagation of flame in a burette 16 or 7 mm. in diameter, are 4.1 and 14.2 percent (190, 195).

BUTYL BROMIDE

The limits of n-butyl bromide in air, with downward propagation of flame in a tube 1.5 cm. in diameter, are 5.2 and 5.6 percent (228).

CHLOROBUTENE

The limits of 2-chlorobutene-2 in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 2.25 and 9.25 percent (138).

ISOCROTYL CHLORIDE

The limits of isocrotyl chloride in (a) air and (b) oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are (a) 4.2 and 19 percent and (b) 4.2 and 66 percent (234).

The limits of isocrotyl chloride in air are apparently about double those of its isomer, chlorobutene. Small differences between the limits of isomers are not unusual, but such a large difference is unique.

ISOCROTYL BROMIDE

The limits of isocrotyl bromide in (a) air and (b) oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at its lower end, are (a) 6.4 and 12 percent and (b) 6.4 and 50 percent (237).

AMYL CHLORIDE

The limits of n-amyl chloride in air, with upward propagation of flame in a closed bomb 4 inches in diameter and 38 inches in length, at a temperature sufficient to volatilize the amyl chloride, are 1.60 and 8.63 percent (138).

The limits of ternary amyl chloride in air, with upward propagation of flame in a 1-inch-diameter tube, open at its upper end and at a sufficient temperature to volatilize the amyl chloride, are 1.50 and 7.40 percent (138).

CHLOROBENZENE; DICHLOROBENZENE

The limits of chlorobenzene and o-dichlorobenzene in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top and at a temperature sufficient to volatilize the substances, are 1.55 and 7.05 percent, and 2.25 and 9.19 percent, respectively (138).

DIMETHYL SULFIDE

The limits of dimethyl sulfide in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 2.25 and 19.70 percent (138).

ETHYL MERCAPTAN

The limits of ethyl mercaptan in air, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are 2.80 and 18.0 percent (155).

DIETHYL SELENIDE

The lower limit of diethyl selenide in air, with downward propagation of flame in a tube 5 cm. in diameter and 65 cm. in length, was 2.81 percent with the tube partly opened during propagation (313) and 2.5 percent with the tube closed (247).

METHYLCHLOROSILANES

Lower limits, with upward propagation of flame in a tube 5.7 cm. in diameter and open at the lower end, are: Dimethyldichlorosilane, 3.4 percent; methyltrichlorosilane, 7.6 percent. The lower limit of one mixture of the two silanes agreed with Le Chatelier's formula (4).

TIN TETRAMETHYL; LEAD TETRAMETHYL

The lower limits of tin tetramethyl and lead tetramethyl in air, with downward propagation of flame in a closed tube 5 cm. in diameter and 65 cm. in length, were 1.90 and 1.80 percent, respectively (315).

PART IV. LIMITS OF MIXED FLAMMABLE GASES AND VAPORS

Part III has covered the limits of flammability of individual flammable gases and vapors. In part IV the limits of mixtures of two or more flammable gases or vapors are given. The chief question is the possibility of using Le Chatelier's law of mixtures (p. 5) to calculate reliable figures for the various mixtures from the ascertained figures for the individual components. This is dealt with in detail in the following pages, but it may be said here that, in general, the law is fairly closely followed by mixtures such as the common fuel gases, and that gross exceptions are observed in many mixtures that contain hydrogen sulfide, carbon disulfide, or vapors such as ether which may give rise to "cool flames."

HYDROGEN AND CARBON MONOXIDE

HYDROGEN AND CARBON MONOXIDE IN AIR

The lower limits of various mixtures of hydrogen and carbon monoxide in air, with upward propagation of flame in a vessel 6 feet high and 12 inches square in section, open at the firing end (64), were as follows:

Lower limits of flammability in a large vessel

Hydrogen	Carbon monoxide	Lower limit, percent		
		Observed	Calculated	Difference
100	0	4.10		
75	25	4.70	4.9	-0.20
50	50	6.05	6.2	-.15
25	75	8.20	8.3	-.10
10	90	10.40	10.4	+.40
0	100	12.50		

In a small vessel 4 cm. in diameter and 25 cm. in length, presumably with downward propagation of flame, the lower limits were as follows (220):

Lower limits of flammability in a small vessel

Hydrogen	Carbon monoxide	Lower limit, percent		
		Observed	Calculated	Difference
100	0	10		
63.9	36.1	11.9	11.5	+0.4
41.5	58.5	13.25	12.8	+.45
18.4	81.6	14.7	14.4	+.3
0	100	15.9		

Other observers obtained similar results in a Bunte burette 19 mm. in diameter, with downward propagation of flame, using a mixture of equal volumes of hydrogen and carbon monoxide (95, 270, 323).

The higher limit in air of a 50:50 mixture of hydrogen and carbon monoxide, with upward propagation of flame in a tube 2 inches in diameter and 5 feet in length, open at the firing end, was 71.8 percent, which is 0.7 percent less than the calculated value (64).

For both limits the differences between the observed figures and those calculated from Le Chatelier's law just exceed the experimental errors.

The limits with downward propagation of flame in a tube 1.6 cm. in diameter have been recorded (17).

Influence of Pressure.—The limits of a mixture containing 51 percent carbon monoxide and 46 to 47 percent hydrogen, in air, were 10.4 and 63 percent at atmospheric pressure and 11 and 78 percent at 800 atmospheres (10).

HYDROGEN AND CARBON MONOXIDE IN OTHER ATMOSPHERES

Atmospheres of Composition Between Air and Pure Oxygen.—The limits of flammability of almost equal volumes of hydrogen and carbon monoxide in atmospheres of nitrogen and oxygen ranging from air to almost pure oxygen have been determined with downward propagation in a burette 19 mm. in width. The lower limit rose slightly from 12.4 percent of the mixture in air to 12.6 percent in oxygen; the higher limit rose from 66.1 percent in air to 82 percent in 98 percent oxygen (323).

Atmospheres of Nitrous and Nitric Oxides. The limits of mixtures of hydrogen and carbon monoxide in nitrous oxide and in mixtures of nitrous and nitric oxides with downward propagation of flame in a 15-mm. burette (335), are plotted in triangular and tetrahedral diagrams, respectively.

Atmosphere of Chlorine.—The limits of certain mixtures of hydrogen and carbon monoxide in chlorine are plotted in a triangular diagram (228).

WATER GAS

The limits of water gas in air, calculated from its chemical composition with the aid of Le

Chatelier's formula for mixtures (p. 5), are in fair agreement with experimental results (*367*).

In some old experiments the limits in air, with upward propagation of flame in a 3-inch-diameter tube, open at its lower end, were 9 and 55 percent (*55*).

The limits of another sample of water gas, with downward propagation of flame in a small tube, were 11.9 and 65.4 percent (*30*).

Still another sample had limits of 6.9 and 69.5 percent in a small bulb compared with 6.1 and 65.4 percent, calculated by Le Chatelier's formula but based on limits of the individual gases obtained in large apparatus. A carbureted water gas under similar conditions had limits of 6.4 and 37.7 percent (*367*).

The limits of various samples of semi-water gas and Mond gas have been determined in a Bunte burette with both upward and downward propagation of flame. Analyses and results are given in the original papers (*269, 270*).

HYDROGEN AND AMMONIA

The limits of mixtures of hydrogen and ammonia in air and in oxygen, with downward propagation of flame, have been determined in small tubes. Apparently the higher-limit mixtures in oxygen give results in fair agreement with Le Chatelier's law (*203*).

HYDROGEN AND HYDROGEN SULFIDE

Both the lower and higher limits of mixtures of hydrogen and hydrogen sulfide in air diverge widely from Le Chatelier's law throughout the whole range of mixtures. The limits are narrower than those calculated, hence limit mixtures of the individual gases when blended produce nonflammable mixtures. The results, obtained in closed tubes 5 cm. in diameter, are plotted in figure 56 for both limits and with upward and downward propagation of flame; the curves calculated from the law are also shown (*357*).

The results that would be obtained if experiments were so conducted that atmospheric pressure was maintained throughout are not known, but it seems unlikely that the wide differences between observed and calculated results would disappear.

HYDROGEN AND METHANE

The lower limits of various mixtures of hydrogen and methane in air, with upward propagation of flame, in a vessel 6 feet high and 12 inches square in section (*57*), were as follows:

Lower limits of flammability of mixtures of hydrogen and methane

Hydrogen	Methane	Lower limit, percent		
		Observed	Calculated	Difference
100	0	4.1	.....	.....
90	10	4.1	4.2	−0.1
75	25	4.1	4.4	−.3
50	50	4.6	4.7	−.1
25	75	4.7	5.0	−.3
0	100	5.6	.....	.....

The higher limit of a mixture of nearly equal volumes of hydrogen and methane in air with upward propagation of flame in a tube 2 inches in diameter and 5 feet in length, open at the firing end, was 22.6 percent (*64*), which is 0.1 percent less than the calculated value based on a corrected higher-limit value (13.8 percent) for methane in the same vessel.

The differences between the observed values and those calculated from Le Chatelier's law are just beyond the experimental error in two instances. Rather greater differences were observed in closed tubes 5 cm. in diameter with upward and downward propagation of flame (*357*).

The approximate limits for mixtures of hydrogen and methane have been determined in a 5-liter bomb with central ignition (*347*) and, for mixtures of equal volumes only, in narrow tubes 0.9 to 0.2 cm. in diameter (*276*).

Influence of Pressure.—The higher limits of mixtures of hydrogen and methane have been determined up to about 50 atmospheres pressure in narrow tubes. The results are undoubtedly low, as those for the two gases separately are low (*51*).

HYDROGEN, CARBON MONOXIDE, AND METHANE

The limits of mixtures of hydrogen, carbon monoxide, and methane in air can be calculated as accurately as those for mixtures of any two of these combustible gases (*64*).

HYDROGEN, CARBON MONOXIDE, AND ETHYLENE

The limits of mixtures of hydrogen, carbon monoxide, and ethylene in air, with downward propagation of flame in a tube 1.6 cm. in diameter, have been determined (*217*).

HYDROGEN, METHANE, AND ETHANE

The limits of all mixtures of hydrogen, methane, and ethane in air can be calculated with approximate accuracy by means of Le Chatelier's law (*146*).
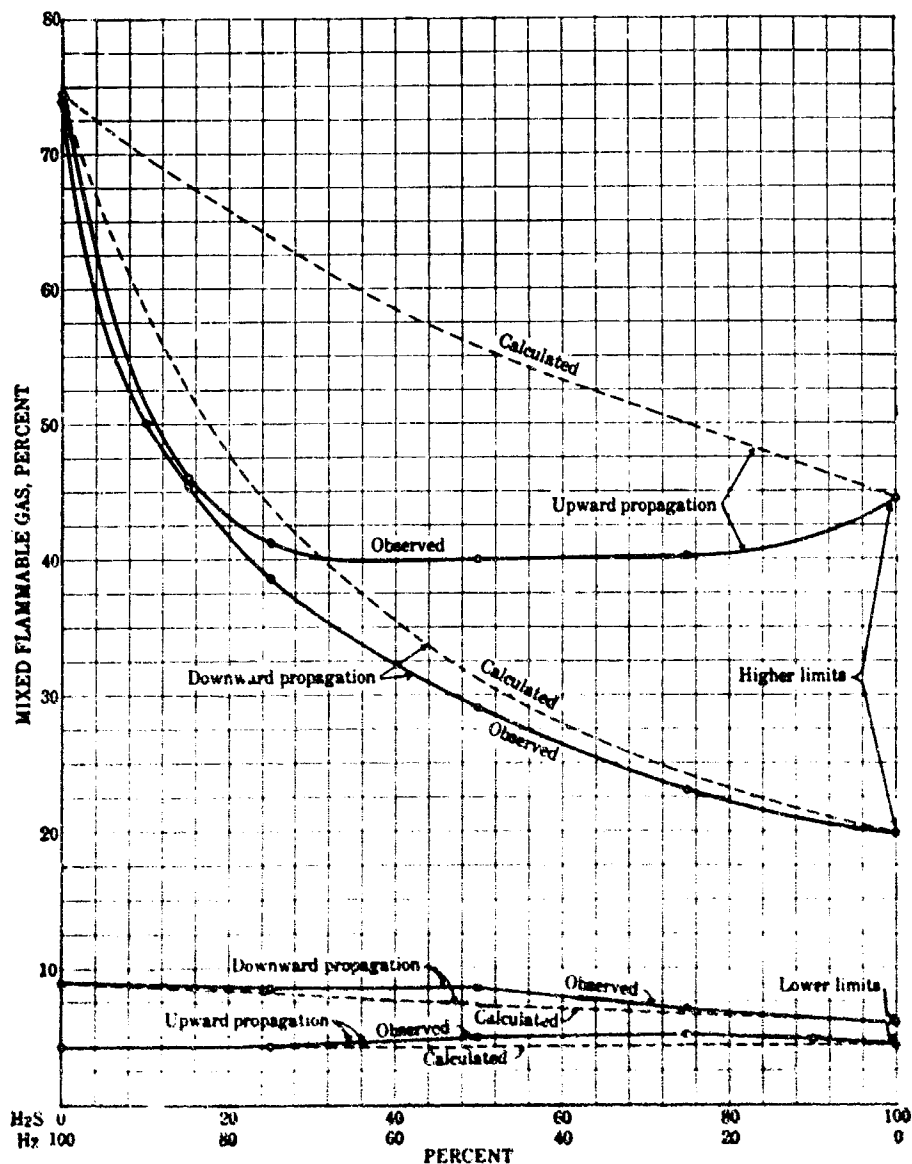
FIGURE 56.   Limits of Flammability of Mixtures of Hydrogen and Hydrogen Sulfide in Air

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).— The limits of all mixtures of these three constituents in air deficient in oxygen or of mixtures of the three constituents with nitrogen in air (or in air deficient in oxygen) can be calculated with approximate accuracy from curves given in figures 1 and 2 or from tabulated results (146).

HYDROGEN AND ETHANE

HYDROGEN AND ETHANE IN OXYGEN

According to an old observation, the higher limit of a mixture of equal volumes of hydrogen and ethane in oxygen, with downward propagation of flame in a eudiometer tube 2 cm. in diameter, is between 56 and 57 percent (243).

HYDROGEN AND PENTANE

The limits for a mixture of 3 volumes of pentane and 2 volumes of hydrogen in air, in a horizontal glass tube 2.5 cm. in diameter with the firing end open, are 2.4 and 8.7 percent (272).

HYDROGEN AND ETHYLENE

HYDROGEN AND ETHYLENE IN AIR

The limits of the entire range of mixtures of hydrogen and ethylene in air, with upward and downward propagation of flame in closed tubes 5 cm. in diameter, were rather narrower than those calculated by Le Chatelier's law; the differences were a few tenths of 1 percent at the lower limits and a few percent at the higher limits (357).

The limits with downward propagation of flame in a tube 1.6 cm. in diameter have been determined (217).

HYDROGEN AND ETHYLENE IN OXYGEN

The limits of mixtures of hydrogen and ethylene in oxygen have been determined in small apparatus (202).

HYDROGEN AND ETHYLENE IN OTHER ATMOSPHERES

Atmospheres of Air and Carbon Dioxide.— The limits of hydrogen and ethylene in various mixtures of air and carbon dioxide have been determined with downward propagation of flame in a tube 1.6 cm. in diameter (217).

HYDROGEN AND ACETYLENE

Lower limits of mixtures of hydrogen and acetylene in air have been determined with upward and downward propagation of flame in closed glass tubes 5 and 7.5 cm. in diameter. With upward propagation and up to about 43 percent acetylene in the hydrogen-acetylene mixture, the lower limits were markedly greater than those calculated; with 43 to 50 percent acetylene the lower limits decreased suddenly, and thereafter the limits almost coincided with the calculated values. With downward propagation the lower limits were consistently a little greater than those calculated (357).

"AMMONIA CONTACT GAS"

The higher limit in oxygen of a mixture prepared for the commercial synthesis of ammonia is 92.2 percent at atmospheric pressure and 94.5 percent at 400 atmospheres. When 5 percent methane is added the limits are 83.7 and 92.8 percent, respectively. No analysis of the contact gas is given (10).

The limits of the mixture $3H_2 + N_2$ in a 500-cc. flask with central ignition are given as 6 and 87 percent in air and 5 and 90 percent in oxygen (328). These figures do not agree with other results on the flammability of mixtures of hydrogen, nitrogen, and oxygen. (See p. 20.)

HYDROGEN AND OTHER GASES OR VAPORS

The limits of a series of binary mixtures of hydrogen and various gases and vapors have been determined with downward propagation of flame in a tube 5 cm. in diameter and 65 cm. in length. The results for each pair of mixtures were of the same general type as those for mixtures of hydrogen and ethyl bromide, which have been quoted on page 22, where their significance is discussed.

The gases and vapors used were ethyl bromide (311); methyl iodide, methylene bromide, bromoform, ethyl iodide, and ethylene bromide (312); hydrogen selenide and diethyl selenide (313); dimethyl selenide and dimethyl telluride (314); tin tetramethyl and lead tetramethyl (315); ethyl alcohol, ether, acetone, benzene, pentane, cyclohexane, methyl cyclohexane, and a hydrocarbon mixture (316).

From a study of the dew point, density, and range of flammability of such mixtures of hydrogen and small quantities of other gases and vapors, it was concluded that tin tetramethyl is the best suppressor of explosions for hydrogen to be used in balloons or airships, followed by dimethyl selenide and ethyl bromide (317). However, the only practical importance of these experiments seems to be the proof that none of the additions is effective in destroying the flammability of hydrogen when it is mixed with air; with 0.90 percent of lead tetramethyl the range of flammability is 9 to 54 percent compared with 9 to 71 percent for pure hydrogen. Moreover, the permeability of a balloon fabric to the explosion suppressors is not considered.

AMMONIA AND ETHYL BROMIDE

The limits of mixtures of ammonia and ethyl bromide in mixtures of oxygen and nitrogen have been determined in very small tubes. A diagram in the original paper shows the limits for ammonia and ethyl bromide vapor singly and mixed; neither gas propagates flame downward when mixed with air, but each will burn in oxygen (204).
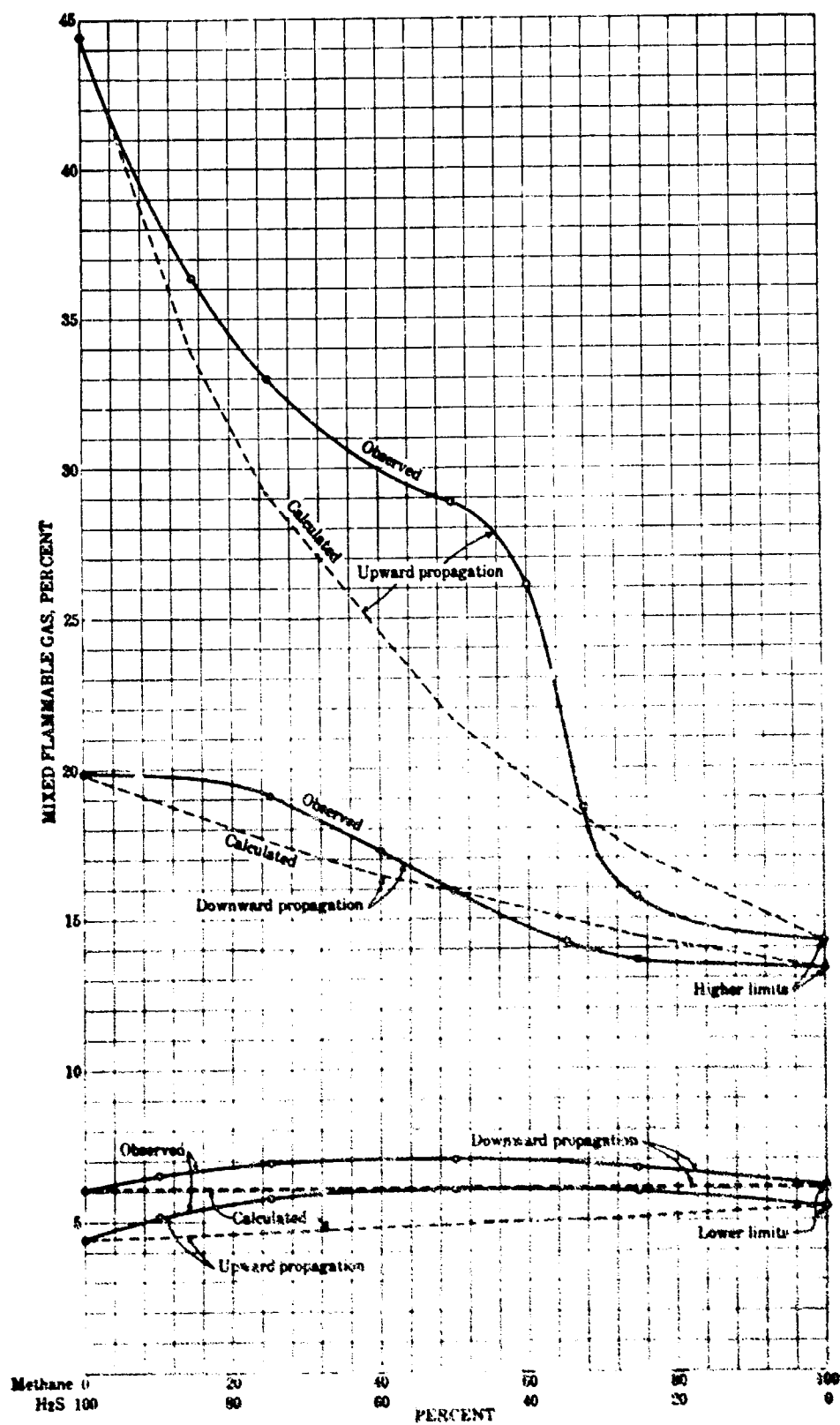
FIGURE 57.—Limits of Flammability of Mixtures of Hydrogen Sulfide and Methane in Air.

HYDROGEN SULFIDE AND METHANE

Both the lower and higher limits of mixtures of hydrogen sulfide and methane in air, with upward and downward propagation of flame in closed glass tubes 5 cm. in diameter, deviate widely from those calculated. The lower limits are markedly high. The higher limits, on the other hand, are very high for mixtures rich in hydrogen sulfide and low for other mixtures of the series, so that the curves (with both directions of propagation) for experimental and calculated figures cut across one another. These curves are reproduced in figure 57 (357).

HYDROGEN SULFIDE AND ACETYLENE

The lower limits of mixtures of hydrogen sulfide and acetylene in air have been determined with upward and downward propagation of flame in closed glass tubes 5 cm. in diameter. The maximum deviation from the calculated limit was 0.3 percent (357).

CARBON DISULFIDE AND VARIOUS GASES AND VAPORS

Neither lower nor higher limits of mixtures of carbon disulfide with ether, benzene, acetone, and acetaldehyde, with downward propagation of flame in closed tubes 5 cm. in diameter and 150 cm. in length, agreed with Le Chatelier's law. It has been suggested that the propagation of flame in mixtures of carbon disulfide and air may be catalyzed by some product of its combustion and that the catalytic effect may be inhibited by ether, benzene, acetone, and acetaldehyde (355).

Mixtures of carbon disulfide with ethyl bromide, diethyl selenide, tin tetramethyl, lead tetramethyl, pentane, and a gasoline fraction boiling at 91.6° C. give abnormal results. The lower limit is raised by the first small additions of these substances, then decreased by larger amounts. The higher limits are at first rapidly reduced, but further additions of some of these substances cause the higher limit to rise (250).

The abnormal effect of small quantities of certain flammable substances on the lower limit of carbon disulfide has already been discussed (p. 29).

CARBON MONOXIDE AND METHANE

The lower limits of various mixtures of carbon monoxide and methane in air in a vessel 6 feet high and 12 inches square in section, with upward propagation of flame at atmospheric pressure (64), were as follows:

Lower limits of flammability of carbon monoxide and methane in air

| Carbon monoxide | Methane | Lower limit, percent | | |
		Observed	Calculated	Difference
100	0	12.5	....	....
90	10	11.0	11.1	−0.1
75	25	9.3	9.6	−.1
50	50	7.7	7.7	0
40	60	7.2	7.1	+.1
25	75	6.4	6.5	−.1
0	100	7.6	....	....

The higher limit of a mixture of equal volumes of carbon monoxide and methane in air, with upward propagation of flame in a tube 2 inches in diameter and 5 feet in length, open at the firing end, was 22.8 percent (64), which is 0.4 percent less than the calculated value based on a corrected higher-limit value (13.8 percent) for methane in the same vessel.

Experiments with downward propagation of flame in a Hempel pipette showed fair agreement with the calculated values for the lower limits of mixtures of carbon monoxide and methane, but for the higher limits the observed values were always low, sometimes as much as 10 percent (46).

Atmospheres of Nitrous Oxide.—The limits of mixtures of carbon monoxide and methane in nitrous oxide, with downward propagation of flame in a 15-mm. burette, have been plotted in a triangular diagram (339).

CARBON MONOXIDE AND ETHYLENE

The limits of mixtures of carbon monoxide and ethylene in air, with downward propagation of flame in a tube 1.6 cm. in diameter, have been determined (217).

CARBON MONOXIDE AND ACETYLENE

The lower limit of a mixture containing 84 percent carbon monoxide and 16 percent acetylene has been determined in a vessel 4 cm. in diameter and 25 cm. in height, presumably with downward propagation of flame from an open end. It was 9.1 percent in air, agreeing closely with the figure calculated from the limits of carbon monoxide and acetylene observed individually under the same conditions (222).

METHANE AND HIGHER-PARAFFIN HYDROCARBONS

METHANE AND ETHANE, METHANE AND PROPANE, METHANE AND BUTANE, AND ETHANE AND BUTANE IN AIR

The lower limits of methane-ethane, methane-propane, methane-butane, and ethane-butane mixtures in air, with upward propagation of

flame in a tube 5 cm. in diameter and open at the firing end, agreed closely with the values calculated from Le Chatelier's law; the higher limits were slightly less than those calculated (74).

The regularity of the lower limits of such mixtures is discussed on page 115.

METHANE AND ETHANE IN MIXTURES OF AIR, NITROGEN, AND CARBON DIOXIDE

The limits of mixtures of methane and ethane in mixtures of air, nitrogen, and carbon dioxide can be calculated closely by the method given on pages 5 to 8, with the aid of figures 1 and 2 (147).

METHANE AND PENTANE IN AIR

Throughout the range of mixtures of methane and pentane the lower limits with upward or downward propagation of flame in a tube 5 cm.

in diameter agree with the limits calculated by Le Chatelier's formula from the limits of methane and pentane separately (357). The lower limit of a 50 : 50 mixture, with horizontal propagation of flame in a tube 2.5 cm. in diameter, open at the firing end, was close to the calculated value (272).

The higher limits in the 5-cm. tube were usually less by a few tenths of 1 percent than those calculated (357).

MIXED PARAFFIN HYDROCARBONS IN GENERAL

The lower limits, but not the higher limits, of the simpler paraffin hydrocarbons and their mixtures exhibit an interesting and useful regularity (74); they are approximately a function of the analytical ratio $C:A$, C being the contraction observed on exploding the mixture with excess air and A the volume of carbon
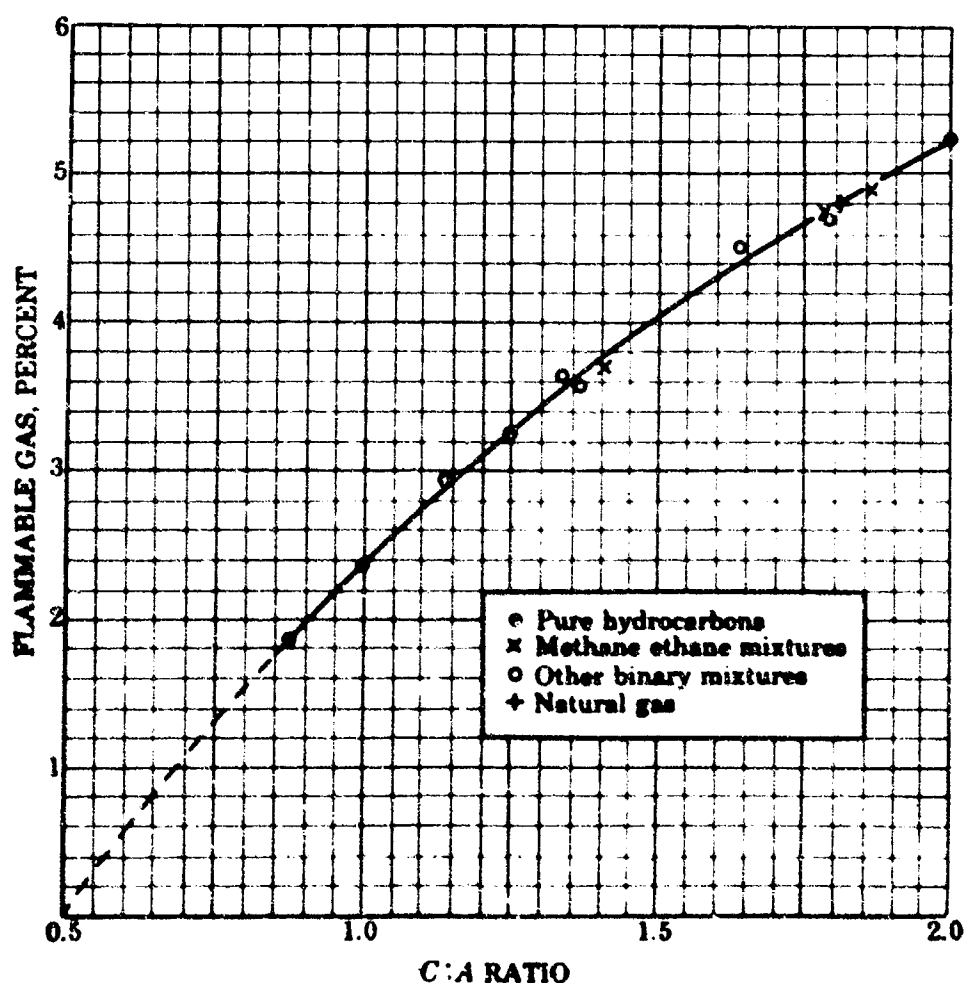
FIGURE 58.—Variation of Lower Limit of Paraffin Hydrocarbons with C:A Ratio.

dioxide produced. The lower limit of any mixture of paraffin hydrocarbons can therefore be deduced without exact knowledge of its composition; all that is required is a determination of the $C:A$ ratio of the mixture and reference to figure 58, the curve of which is drawn through experimental points. The broken part of the curve may be used to supply the lower limits of heavy paraffin hydrocarbons and of their mixtures.

Recent figures for the higher hydrocarbons confirm the curve, but figures for ethane and propane tend to flatten it somewhat.

NATURAL GAS

NATURAL GAS IN AIR

The lower limit of a natural gas in air, with upward propagation of flame in a tube 7 feet in height and 12 inches in diameter and with the firing end open, was 4.81 percent. The mixture contained about 2 percent water vapor. The percentage composition of the gas was: Methane, 87.4; ethane, 6.8; propane, 1.55; butane, 0.81; pentane, trace; nitrogen, 3.2; oxygen, 0.1; and carbon dioxide, 0.0. The limit figure represents, for convenience, the proportion of the flammable constituents of the natural gas in the limit mixture with air. If the nitrogen and oxygen were included, the limit would be nearly 5.1 percent. For propagation of flame upward from closed to open end in the same tube, the lower limit was 4.74 percent (flammable constituents).

The limits of the same natural gas with upward propagation of flame in a tube 2 inches in diameter, open at the firing end, very nearly obey Le Chatelier's law. For dry gases the limits of the flammable part of the natural gas were 4.80 and 13.46 percent. The figures calculated from the corresponding limits for the individual constituents methane 5.24 and 14.02 percent; ethane 3.22 and 12.45 percent; propane 2.37 and 9.50 percent; and butane 1.86 and 8.41 percent were 4.85 and 13.72 percent. The lower limit is not appreciably affected by the nitrogen in the natural gas, but the higher limit is (compare fig. 20, showing the influence of nitrogen on the limits of methane in air). An estimate of the influence of nitrogen on the higher limit may be made thus: If 0.4 percent nitrogen is deducted (which corresponds with 0.1 percent oxygen found in the natural gas) there remains 2.8 percent nitrogen, which is brought to the mixture with the natural gas. As this amount is present with the 13.7 percent hydrocarbons in the whole limit mixture, it represents about 0.4 percent "additional nitrogen" in the original "atmosphere." Figure 20 shows that this depresses the higher limit of methane about 0.1 percent, and doubtless its

effect on the higher limit of natural gas is about the same (74).

Further evidence that the limits of natural gas may be calculated fairly accurately from the limits of its various constituents is provided by data showing that Le Chatelier's law is followed when certain pairs of the constituents are taken together. (See the sections on methane-ethane, methane-propane, methane-butane, methane-pentane, and ethane-butane mixtures.) The limits of 22 samples of "natural gas," of widely varying compositions from many States, have been calculated on the basis of analytical figures expressing the flammable constituents as methane and ethane only (154).

Influence of Pressure.—In experiments in a closed tube 2 inches in diameter and 12 inches in length, with upward propagation of flame and with initial pressures from 1 to about 24 atmospheres, the lower limit of a natural gas (analysis: Methane, 79.6; ethane, 19.2 percent) remained nearly constant; the higher limit rose from 14.0 to 37.5 percent (154). In an extension of these experiments, but with a tube 15 inches long and a natural gas giving by analysis methane around 85 percent and ethane around 15 percent, the following figures may be read from plotted results (160):

Initial pressure, lb. per in.²	Atmospheric	500	1,000	2,000	3,000
Lower limit	4.50	4.45	4.30	3.40	3.15
Higher limit	14.2	44.2	52.9	59.0	60.0

In narrow tubes (3 or 5 mm. in diameter) with downward propagation of flame, the higher limit of a "natural methane" (methane, 80.3; higher paraffins, 11.1 percent) rose from 14.25 percent "methane" at atmospheric pressure to 39 percent at 12 atmospheres and 52 percent at 50 atmospheres (281).

At pressures below atmospheric, in a closed tube 2 inches in diameter and 6 feet in length, with upward propagation of flame, the limits remained nearly constant as the initial pressure was reduced from atmospheric to about 200 mm. At lower pressures the limits converged and propagation was not obtained below 50 mm. (154).

Influence of Turbulence Caused by Fans or by the Detonation of Explosives.—Experiments have been made to determine whether the lower limit of natural gas in air is affected by turbulence such as that produced by fans or by the detonation of explosives (75). The use of explosives necessitated experiments on a rather large scale; therefore a 20-foot section of a 100-foot steel tube 6½ feet in diameter was used. The explosives were fired near one end of the horizontal axis of the tube. The tube had paper-covered relief vents along the top, and

the end opposite the source of ignition was closed by a paper cover. The appearance of flame at the various orifices enabled the extent of an inflammation to be roughly judged. The observations were aided by noting the effect of an experiment on tufts of guncotton placed at various points in the tube.

The results were conveniently classed as (1) explosions, when the paper covers were blown out violently and flame appeared from the vents; (2) inflammations, when it was evident that some gas had been ignited, but no great violence was observed; and (3) nonignitions.

A small electric igniter of black blasting powder gave a lower limit of explosion of about 5.6 percent natural gas and a lower limit of inflammation of about 4.6 percent.

Black blasting powder (50 or 200 grams), burning with a long flame, gave limits of 5.1 percent and less than 4.7 percent, respectively.

A straight nitroglycerin dynamite (50 or 200 grams) gave a lower limit of explosion of 5.6 percent; "inflammation" could not be observed with certainty at lower percentages on account of the violent effects of the detonation on the paper covers.

Turbulence induced by a fan run at appropriate speeds reduced the limit of explosion to 5.0 percent. The limit of inflammation was reduced slightly at moderate speeds; at higher speeds inflammation, apart from explosion, could not be observed.

The term "inflammation", as used in the preceding paragraphs, apparently covered the range of mixtures capable of propagating flame from the source of ignition for some distance upward, spreading more or less laterally; the term "explosion" was used to designate enough inflammation at sufficient speed to cause the effects described. The reduction of the limit of explosion by the long flames of gunpowder was due to the greater burning induced by them; a similar effect was produced by turbulence.

The natural gas used in these experiments contained 87.8 percent methane, 6.9 percent ethane, 2.6 percent propane, 0.8 percent butane, 1.9 percent nitrogen, and no oxygen or carbon dioxide. The percentages of natural gas in the limit mixtures refer to "nitrogen-free" gas (75).

NATURAL GAS IN OTHER ATMOSPHERES

Atmospheres of Air, Nitrogen, and Carbon Dioxide.—An extensive series of experiments in a 100-cc. Hempel pipette and in a short steel cylinder of 2.8-liter capacity has been made with one sample of natural gas (Pittsburgh)
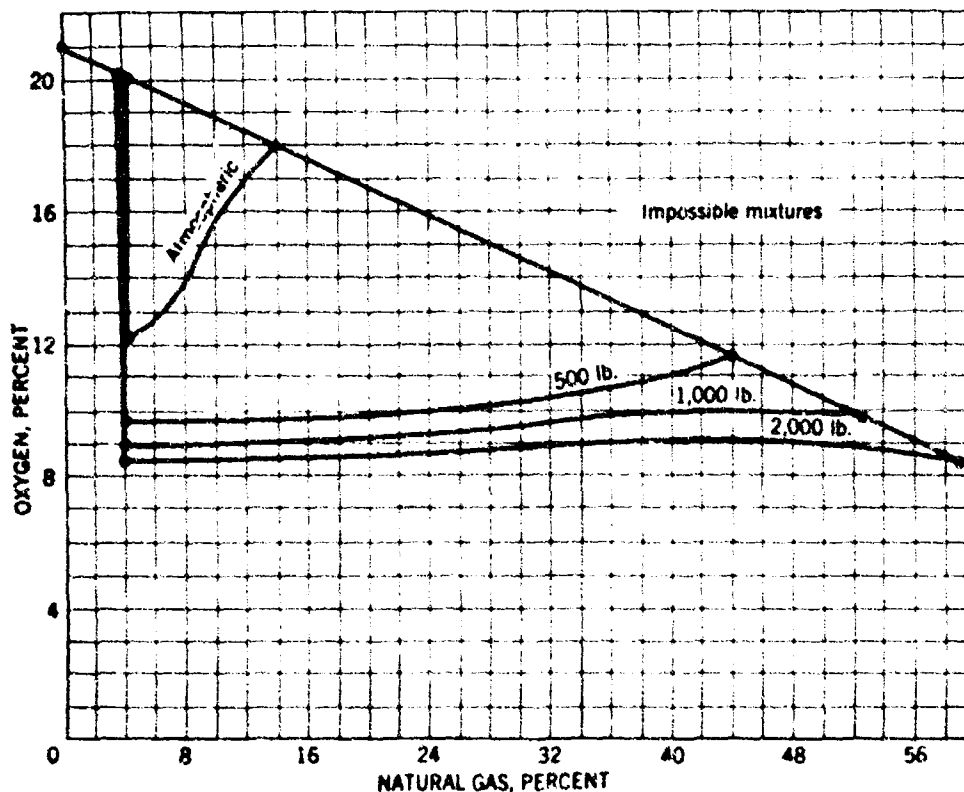
FIGURE 59.   Oxygen Content of Flammable Natural Gas-Air-Nitrogen Mixtures at High Pressures.

and atmospheres that contained oxygen, nitrogen, and carbon dioxide. The composition of the mixtures tested, including the natural gas, ranged from 19.9 to 14 percent oxygen and from 0 to 61 percent carbon dioxide. The results are plotted in comprehensive curves in the original paper (54).

The limits of any sample of natural gas containing methane, ethane, propane, butane, nitrogen, and carbon dioxide can be calculated with reasonable accuracy from the limits of the individual combustible constituents in atmospheres of different oxygen and carbon dioxide content (147). The experiments were made in a tube 2 inches in diameter and 6 feet in length, with upward propagation of flame at atmospheric pressure

Atmospheres of Air and Nitrogen at Elevated Pressures.—The limits of a natural gas (methane, 85 percent; ethane, 15 percent) in air-nitrogen mixtures at elevated pressures have been determined, with upward propagation of flame in a tube 2 inches in diameter and 15 inches in length. The results are summarized in figure 59, from which may be ascertained whether any such mixture, of known natural gas and oxygen content, is flammable at the various pressures indicated (160). Interpolation, or reference to other diagrams in the original paper, will give the same information for other pressures.

METHANE AND ETHYLENE

The limits of mixtures of methane and ethylene in air, with upward and downward propagation of flame in closed tubes 5 cm. in diameter, were generally slightly narrower than those calculated (357).

METHANE AND ACETYLENE

The limits of mixtures of methane and acetylene in air with upward and downward propagation of flame have been determined in closed glass tubes 5 cm. in diameter. The lower limits with both directions of propagation were slightly higher than those calculated. The higher limits with downward propagation were a little less than those calculated, but with upward propagation they were much greater. The greatest difference was shown by the 40:60 acetylene-methane mixture, for which the observed higher limit was 47 percent compared with 21 percent for the calculated higher limit (357).

METHANE AND CERTAIN HALOGENATED HYDROCARBONS

For the limits of mixtures of methane with certain halogenated hydrocarbons which are either flammable separately, or become flammable when mixed with methane, see pp. 51 to 54.

METHANE AND VARIOUS VAPORS

The complete ranges of flammability of methane and the vapors of various substances have been determined individually in air with downward propagation of flame in narrow tubes. These substances are: Isobutyl chloride, propyl bromide, ethyl iodide, sulfuryl chloride, silicon tetrachloride and silicochlorcform (195), and isoamyl bromide (196).

Atmosphere of Oxygen.—Representative series of experiments on the limits of mixtures of methane and methyl chloride in oxygen have been made at pressures from 600 mm. down to the point of coincidence of the limits (89).

BUTANE AND ETHYL CHLORIDE

The limits of mixtures of butane and ethyl chloride in air, with downward propagation of flame in a 1.6-cm.-diameter tube, are given in curves (340).

BENZINE

BENZINE IN AIR

The lower limit of benzine in air with upward propagation of flame in a tube 6.2 cm. in diameter, open at the firing end, was 1.1 percent. The limits for propagation downward in a closed pipette 1.9 cm. in diameter were 2.4 and 4.9 percent. All the benzine distilled below 165° C. (95). In similar experiments to the last named, a second observer found limits of 1.9 and 5.1 percent for benzine having a boiling range of 67° to 94° C. (343).

BENZINE IN OTHER ATMOSPHERES

Atmospheres of Composition Between Air and Pure Oxygen.—The lower limit of benzine in all atmospheres of composition between air and pure oxygen, with downward propagation of flame in a Bunte burette 19 mm. in diameter, was about 2.0 percent; the higher limit rose from 5.1 percent in air to 19 percent in 60 percent oxygen and 28.6 percent in 94 percent oxygen (343).

Atmospheres of Air and Carbon Tetrachloride.—Large amounts of carbon tetrachloride must be added to benzine in order that the vapors arising from the liquid shall be incapable of forming a flammable mixture with air (7).

BENZINE AND BENZENE

Influence of Pressure.—Curves showing the influence of pressure up to 500 atmospheres on the limits of a 60:40 mixture of benzine

(boiling range, 78°–82°) and benzene in air have been given (*11*). but the range of flammability seems impossibly wide.

GASOLINE (PETROL)

GASOLINE IN AIR

The limits of three gasolines, with upward propagation of flame in a 2-inch-diameter tube at approximately atmospheric pressure, have been determined (*141*). The gasolines had the following properties:

Sample	Octane rating	Specific gravity at 60/60° F	Vapor pressure ... in. Hg at 220° C.
1	74	0.736	.90
2	82	.761	182
3	100	7.61	168

Tests of the flammability of mixtures were made alternatively by applying an alcohol flame at the open lower end of the tube, or by passing a spark just within the lower end of the tube without removing the ground-glass cover-plate. When the latter procedure was used, the mixture was originally at a reduced pressure but the passage of flame raised the pressure to approximately atmospheric. The results obtained by the two methods were nearly the same, as is shown by the following figures.

Sample	Limits of flammability in air, percent by volume			
	Tube ... flame ignition		Tube ... spark ignition	
	Lower	Higher	Lower	Higher
1	1.50	7.6	1.40	7.5
2	1.50	7.6	1.45	7.4
3	1.45	7.4	1.40	7.1

The limits in air may therefore be put as 1.4 and 7.6 percent (*141*).

Other determinations of the limits of gasoline vapor in air are as follows:

The limits with upward propagation of flame in a 2.8-liter glass jar were 1.45 and 6.2 percent gasoline vapor (by volume). The limits with downward propagation in a Hempel pipette of 100-cc. capacity were 1.95 and 5.25 percent; with upward propagation the lower limit was 1.55 percent. The gasoline had a specific gravity of 0.689 at 15° C. and a boiling range of 50° to 140° C.; at 140° C. there was 2.7 percent residue (*41, 42*).

The limits in a cylindrical bomb of 12 liters capacity were 1.4 and 6.0 percent (*256*).

The lower limits of five gasolines in a small test tube ranged from 1.24 to 1.64 percent; the

higher limits from 5.42 to 7.88 percent (*524*).

The lower limits, by weight, of the more-volatile parts of a series of cracked and straight-run gasolines are equal (*296*). This is explained by the observation that the limits of *n*-hexane, *n*-heptane, *n*-octane, cyclohexane, and benzene are equal, 57 mg. per liter of air (*36*).

The limits of gasolines obtained by the distillation of raw oils up to 180° C. have been determined in a 2.3-liter bottle. The oils are described as Irak, Pechelbronn, Kettleman Hills, Equateur, Saxet, and Santa-Fé. The results are expressed in terms of cubic centimeters of liquid per liter of air at 100° C., and the maximum differences were 11 percent in the lower limit, 14 percent in the higher limit (*231*).

Influence of Pressure. — At pressures below atmospheric, in a closed tube 2 inches in diameter and 6 feet in length, with upward propagation of flame, the limits of a gasoline (100-octane) remained nearly constant as the initial pressure was reduced from atmospheric to about 300 mm. At lower pressures the limits converged, and propagation was not obtained below 35 mm. pressure (*180*). In a tank of 125 cubic feet capacity, the limiting pressure, at which no propagation of flame was obtained in any mixture of gasoline and air, was about 33 mm. (*257*).

In another series of experiments, which seem to have been tests of the incendivity of various sparks rather than determinations of limits of flammability, ignition was not obtained, in a 4.19-liter spherical vessel, below 100 mm. (*259*).

Influence of Temperature. — At 400° C. the lower limit with upward propagation of flame in a Hempel pipette of 100 cc. capacity was 1.1 percent compared with 1.55 percent at room temperature (*71*).

Other experiments indicate that temperature has a greater effect; but the results seem unreliable because in a parallel series of tests the lower limit of alcohol at room temperature was undoubtedly too high (*90*).

The lower limits of some French gasolines, with downward propagation of flame in a 2½-liter bottle, at temperatures from 100° to 250° C., are given in table 41 (p. 126).

Experiments in a 4.19-liter spherical vessel, at 1,000 mm. pressure, gave the limits of an 87-octane gasoline as 1.1 and 7.6 percent at 0° C., 1.35 and 7.1 percent at 46.5° C. Other results are represented in a series of diagrams (*259*).

The lower limits of a gasoline (distillation range, 58° to 131° C.) with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39 cm. in length, vented at its upper end, are 1.07 percent at 21° C., 0.94 at 100° C., and 0.77 at 200° C. (*259*).

GASOLINE IN OTHER ATMOSPHERES

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen).—The limits of the three gasolines defined above (*see* Gasoline in Air, samples 1, 2, and 3), with upward propagation of flame in a 2-inch tube at approximately atmospheric pressure, are given by a single curve (N_2) in figure 60. No mixture of gasoline vapor, air, and nitrogen is flammable if it

Atmospheres of Air and (a) Trichloromonofluoromethane, (b) Dichlorodifluoromethane, and (c) Dichloromonofluoromethane.—Figure 60 also shows the results of similar experiments with these three halogen-substituted methanes. Their extinctive effects are considerably greater than those of nitrogen and carbon dioxide, and no mixture of gasoline vapor, air, and any of them which contains less than 17.2 percent of oxygen is flammable (*141*).
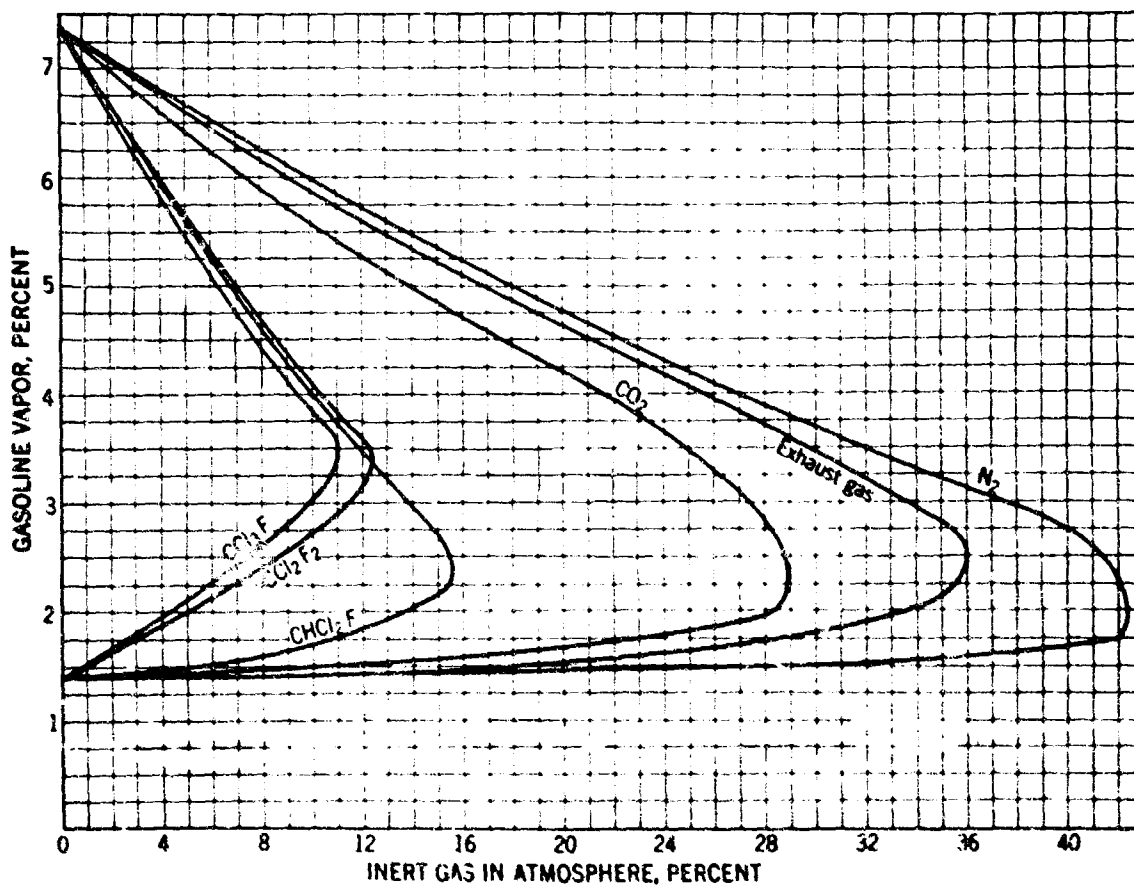
FIGURE 60. Limits of Flammability of Gasoline Vapor in Various Air-Inert Gas Atmospheres.

contains less than 11.6 percent of oxygen (*141*).

Atmospheres of Air and Carbon Dioxide.—Figure 60 also shows the limits of gasoline vapor in all mixtures of air and carbon dioxide, determined as in the previous paragraph (*141*).

Atmospheres of Air and Exhaust Gas.—Figure 60 also shows the limits of gasoline vapor in all mixtures of air with a mixture containing 85 percent of nitrogen and 15 percent of carbon dioxide, that is, an "exhaust gas" of a petrol engine with the fuel-air ratio adjusted to give a maximum of carbon dioxide and a minimum of carbon monoxide and oxygen (*141*).

Atmospheres of Air and Carbon Tetrachloride.—*See* table 20.

NAPHTHA

The limits of naphtha (distillation range, 146° to 171° C.) in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top and at a temperature sufficient to vaporize the naphtha, are 0.83 and 4.85 percent (*138*).

Influence of Temperatures.—The lower limits of three types of naphtha in air at various

temperatures, with upward propagation of flame in a steel cylinder 30.6 inches in diameter and 39 cm. in length, vented at its upper end, are given below (239):

	High-solvency petroleum naphtha	No. 10 mineral spirits	VM & P
Distillation range....	104° to 137° C.	155° to 196° C.	97° to 155° C.
Specific gravity.....	0.8129	0.7816	0.488
Flash point..........	2.5° C.	40.0° C.	−2.5° C.
Lower limits at the following temperatures, ° C.:			
21.................	1.00		0.92
100................	0.89	0.77	0.76
200................	0.74	0.63	0.67
225................	0.72	Preflame combustion	Preflame combustion
250................	0.69	do.	Do.

NAPHTHA IN OTHER ATMOSPHERES

Atmospheres of Air and Carbon Tetrochloride.—See p. 68.

KEROSINE

The limits of kerosine in air, with upward propagation of flame in a tube 1 inch in diameter and 18 inches in length, open at the top and at a temperature sufficient to vaporize the kerosine, are 0.76 and 4.80 percent (138).

PETROLEUM VAPORS

The limits of the vapors arising from a crude petroleum (flash point −21° C., boiling range 61° to 313° C.) were 1.3 and 4.9 percent with downward propagation of flame in a small vessel. Above 5° C. air saturated with the vapors was above the higher limit of flammability (229).

The limits for the higher fractions of petroleum (that is, Diesel oils) lie in a range up to about 56 mg. per liter even when the oil is suspended as a fine mist at ordinary temperatures (36).

Atmospheres of Air and Carbon Dioxide.— The addition of carbon dioxide to the atmosphere narrowed the limits until they coincided: at 5° C., 61 percent carbon dioxide was necessary; at 20°, 51 percent; at 30°, 44 percent; and at 40°, 37 percent (229).

CYCLOPROPANE AND ETHYLENE

CYCLOPROPANE AND ETHYLENE IN OXYGEN

The higher limits of mixtures of cyclopropane and ethylene in oxygen, with upward propagation of flame in a 2-inch-diameter tube, open at the lower end, are given in table 39 (163).

TABLE 39.—Higher limits of mixtures of cyclopropane and ethylene in oxygen

Composition, percent by volume			Composition, percent by volume		
Cyclopropane	Ethylene	Oxygen	Cyclopropane	Ethylene	Oxygen
60.0	0	40.0	19.2	54.3	26.5
45.4	15.1	39.5	11.0	66.6	22.4
38.2	25.3	36.5	0	79.9	20.1
28.8	40.7	30.5			

CYCLOPROPANE AND ETHYLENE IN OTHER ATMOSPHERES

The addition of 10 percent of helium to cyclopropane-ethylene-oxygen mixtures affects the minimum oxygen content for flame propagation only slightly. Similarly, the addition of 10 percent of hydrogen had little effect (163). The addition of nitrogen, up to 20 percent, "is of no particular advantage in reducing flammability, nor does such addition permit mixtures of a higher oxygen content to be used in anesthesia if nonflammability is required" (163).

DIMETHYL CYCLOPENTANE AND ISOHEPTANE

The lower limit of a mixture of 43 percent dimethyl cyclopentane and 57 percent isoheptane, with downward propagation of flame in a tube 5 cm. in diameter at 145 cm. in length, open at the firing end, is 1.12 percent (250).

TURPENTINE

The lower limit of turpentine in air, conditions not specified, is 0.8 percent (101).

Influence of Temperature.— The lower limits of turpentine (distillation range, 153° to 197° C.) with upward propagation of flame in a cylinder 30.6 cm. in diameter and 39.0 cm. in length, vented at its upper end, are 0.69 percent at 100° C. and 0.54 at 200° C. (239).

COAL GAS AND COKE-OVEN GAS

COAL GAS AND COKE-OVEN GAS IN AIR

The lower limit of a "town gas" (64), with upward propagation of flame in a vessel 6 feet high and 12 inches square in section, open at the firing end, was 5.35 percent. The figure calculated from an analysis given below in conjunction with the limits of the individual constituents of the gas is 5.36 percent.

The higher limit of a coal gas (64), with upward propagation of flame in a tube 5 feet in height and 2 inches in diameter, open at the firing end, was 30.9 percent. The calculated

figure is 28.8 percent, uncorrected for inert constituents of the gas.

The limits of coke-oven gas, with upward propagation of flame in a 6-cm.-diameter tube, loosely stoppered, were 4.4 and 34.0 percent (280).

The compositions of the town gas, coal gas, and coke-oven gas used in the foregoing experiments were given as follows, in percentages:

Reference	Town gas (53)	Coal gas (6.)	Coke-oven gas (280)
Benzene, etc.	0.8	1.2	....
Carbon dioxide	2.6	.1	....
Oxygen	.5	.1	0.2
Ethylene, etc.	2.8	2.9	1.5
Carbon monoxide	14.1	7.3	8.1
Hydrogen	46.6	50.6	61.2
Methane	19.4	29.7	25.6
Ethane	4.0	3.2	....
Nitrogen	9.2	4.9	6.4

The recorded limits of town and coal gas in smaller vessels and for other directions of propagation are such as might be expected from mixtures containing a large proportion of hydrogen and different amounts of heavy hydrocarbons (9, 24, 28, 30, 43, 55, 95, 218, 241, 270, 276, 281, 297, 323, 367, 368). Thus, for the lower limit the figures range from 5 percent for upward to 10 percent for downward propagation; the higher-limit figures range from 18.5 percent for downward to 31 percent for upward propagation. One higher limit given is 53.8 percent; the composition of the gas is not stated (9).

An old set of comparative experiments showed an increase from 8.1 to 8.7 percent in the lower limit of a coal gas as the diameter of the experimental tube was decreased from 30 to 10 mm. (218). More recent experiments showed that flame would still travel, apparently indefinitely, in a tube 3 mm. in diameter when one of the most explosive mixtures was used but would not travel in a tube 2 mm. in diameter (276).

Influence of Pressure.—The higher limit of a French town gas rose rapidly with increasing pressure. At atmospheric pressure the higher limit was 18.5, at 10 atmospheres 37.5, and at 22 atmospheres 51 percent. Further increase in pressure had less effect, as at 54 atmospheres the limit was 56.5 percent gas. The experiments were made with gas compressed into tubes of 3- or 5-mm. diameter, with downward propagation of flame, and reasons are given for concluding that the results would be the same in wider vessels (281). However, as similar experiments (51) gave low results for hydrogen and for methane these results also are probably too low. Moreover, for upward propagation of flame the results would probably be higher. The observations are of importance in relation to the use of compressed gas (281).

Influence of Temperature.—In a 35-cc. bulb, with side ignition, the lower limit fell gradually from 6.9 to 6.3 percent, and the higher limit rose from 22.8 to 28.7 percent as the temperature was increased from 15° to 300° C. The composition of the gas used is given under the heading Coal Gas in Oxygen (297).

Influence of Impurities (Nitrogen and Carbon Dioxide).—Two curves in figure 61 show the limits of a coal gas polluted with nitrogen and carbon dioxide, with downward propagation of flame in a Bunte burette. The abscissas represent the composition of the gas in terms of its calorific value (30). These can readily be converted to percentage composition, as the calorific value of each mixture is proportional to its coal-gas content.

COAL GAS IN OXYGEN

The limits of coal gas in oxygen in a 35-cc. bulb, with side ignition, were 7.4 and 69.7 percent (297). The percentage composition of the coal gas was: Heavy hydrocarbons, 5.3; carbon dioxide, 2.0; carbon monoxide, 6.4; methane, 34.5; hydrogen, 49.4; and nitrogen, 2.4.

Influence of Temperature.—In the same series of experiments it was found that, as the temperature was raised to 300° C., the lower limit fell gradually to 6.9 percent and the higher rose to 72 percent.

Influence of Pressure.—The higher limit of a French town gas in oxygen was 78.6 percent at atmospheric pressure, 85 percent at 10 atmospheres, and 89.1 percent at 43 atmospheres. The experiments were performed as described under Coal Gas in Air. At 74 atmospheres pressure a mixture of 89.6 percent gas and 10.4 percent oxygen could not be exploded. It was concluded that mixtures of town gas and oxygen, compressed in tanks up to 200 atmospheres pressure, could not explode if they contained less than 10 percent oxygen but that it would be prudent not to exceed 5 or 6 percent oxygen. Moreover, such mixtures must be compressed in such a way as to avoid undue rise in their temperature, which would widen the limits. Up to 80° C., however, the higher limit is not appreciably altered (50, 281).

COAL GAS IN OTHER ATMOSPHERES

Atmospheres of Composition Between Air and Pure Oxygen.—The limits of a synthetic illuminating gas in air in a Bunte burette were 9.7 and 25.1 percent; they rose to 9.9 and 73.7 in a mixture of 96 percent oxygen and 4 percent nitrogen (323). The percentage composition of the gas used was: Carbon dioxide, 2.0; ethylene, 3.8; carbon monoxide, 9.0; methane, 30.2; hydrogen, 51.0; and nitrogen, 4.0.
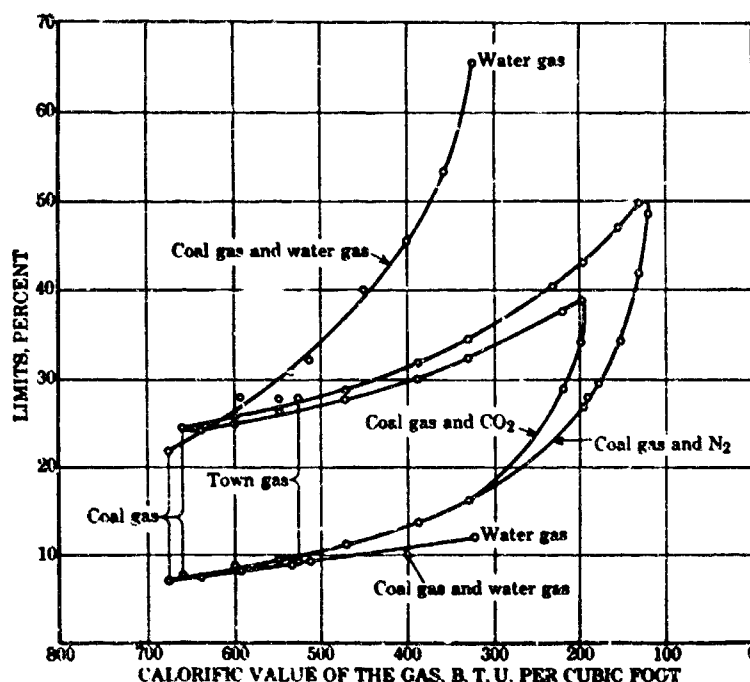
FIGURE 61.—Limits of Flammability of Coal Gas With Various Admixtures.

Atmospheres of Air and Nitrogen (Air Deficient in Oxygen) and Air and Carbon Dioxide.—From the data in figure 61 calculations may be made of the composition of the atmosphere which, in a small burette, is just incapable of forming a flammable mixture with coal gas. If the air contains less than 11.5 percent oxygen it cannot form a flammable mixture with coal gas; if the oxygen content is reduced by the addition of carbon dioxide, then when the mixture contains more than 31 percent carbon dioxide, and, consequently, less than 14.4 percent oxygen it cannot form a flammable mixture with coal gas. These results are in close agreement with the analytical figures of an old observation (95). These conclusions may be fairly representative of a normal coal gas, but they are based on observations of flame traveling downward in a narrow burette; in wider vessels, especially when ignition occurs near the lower part of the vessel, the oxygen figures would doubtless be several percent less.

Atmospheres of Air and Water Vapor. The limits of mixtures of a typical coal gas and air standing over water in a 350-cc. spherical vessel, and ignited near the water surface, have been determined at various temperatures. As the temperature rises, and consequently the water-vapor content also, the lower limit rises slowly and the higher limit falls rapidly, as with other diluents. When about 42 percent

of water vapor is present the limits coincide at about 8.4 percent coal gas (368).

Atmospheres of Air and Methyl Bromide.—The addition of increasing amounts of methyl bromide to the air causes the limits of a coal gas (composition given in the original) to approach and, in a 2-inch-diameter tube, to meet when 11.0 percent of the mixture is methyl bromide (38). For a comment, compare the corresponding paragraph on hydrogen (p. 22).

The limits of coal gas in mixtures of air and methyl bromide have been calculated, by the method given on page 5, from the limits of its components in air and in mixtures of air and methyl bromide. The agreement with the experimental results is good for lower limits, moderately so for higher limits (38).

Atmospheres of Oxygen and Carbon Dioxide.—The limits of coal gas in an atmosphere composed of 21 percent oxygen and 79 percent carbon dioxide, in a 35-cc. bulb with side ignition, were 7.6 and 25.2 percent. At 300° C. the limits were 9.3 and 18.2 percent. The composition of the gas used is given under the heading Coal Gas in Oxygen (297).

COAL GAS AND METHANE

The lower limits of mixtures of coal gas and methane, with downward propagation of flame, can be calculated from the limits of coal gas and methane separately (218).

COAL GAS AND WATER GAS

Figure 61 shows the limits in air of all mixtures of a typical coal gas and a water gas, with downward propagation of flame in a Bunte burette (*30*). The abscissas represent the composition of the gas in terms of its calorific value. The addition of water gas to coal gas widens the range of flammability and consequently increases the chance of an explosion. With upward propagation of flame the range would doubtless be wider at each limit by several percent.

MINE-FIRE GASES AND GASES FROM MINE EXPLOSIONS

Although mine-fire gases and atmospheres after explosions vary greatly in composition their limits of flammability may be calculated with approximate accuracy by the method given on page 5. Examples (*133*) are given in table 40.

If the atmospheres contain methane and negligible quantities of hydrogen and carbon monoxide, approximate limits can be obtained from figure 22 (p. 47).

TABLE 40.— *Typical samples of mine-fire atmospheres in coal mines*

Sample No.	Composition of atmosphere, percent by volume						Limits of flammability	
	CO_2	O_2	CO	CH_4	H_2	N_2	Lower	Higher
1	13.8	2.8	4.3	3.3	4.9	70.9	15.1	70.4
2	1.6	11.1	1.0	7.2	0	76.1	69.2	100.0
3	.5	17.4	0	12.6	0	69.5	40.1	100.0
4	1.3	17.0	1.9	4.0	0	75.8	(¹)	(¹)
5	6.4	1.4	1.1	16.7	.2	74.2	30.5	41.3
6	5.9	1.4	1.4	22.3	0	69.0	23.1	37.9
7	2.6	8.8	0	8.1	0	80.5	(¹)	(¹)

¹ Nonflammable.

AUTOMOBILE EXHAUST GAS

The usual adjustment of an automobile carburetor gives an air:fuel ratio of about 12.5:1 by weight, and the exhaust is nonflammable. If, however, the air:fuel ratio is reduced below about 11.7:1 the exhaust is flammable, and there is danger of an explosion as well as of carbon monoxide poisoning when the engine is run in a poorly ventilated place. The limits of flammability of the exhaust gas may be calculated with approximate accuracy by the method given on page 5 (*131, 133*).

BLAST-FURNACE GAS

The limits of two typical blast-furnace gases, with upward propagation of flame in a glass tube 2 inches in diameter and 6 feet in length, open at the firing end, were 36 and 72 percent and 35 and 73.5 percent. These figures agree approximately with those calculated from the quantities and limits of the component gases by the method given on p. 5 (*133*).

The limits of a blast-furnace gas in a closed tube 3 inches in diameter and 8½ inches in length, with central ignition, are 45 and 65 percent (*43*). In a Bunte burette the limits were 35.8 and 71.9 percent with upward

propagation and 43.9 and 67.8 percent with downward propagation of flame (*269*).

The composition of the gases used in the preceding experiments was, in percentages:

Reference	(*131*)		(*43*)	(*269*)
	(a)	(b)		
Carbon dioxide	13.90	8.30	10.0	8.2
Oxygen	0	0	.5	0
Carbon monoxide	28.70	30.65	27.5	25.6
Methane	.50	10	.3	0
Hydrogen	4.30	4.00	2.7	4.4
Nitrogen	52.90	57.95	59.0	61.8

PRODUCER GAS

The limits of producer gas in a Bunte burette were 35.5 and 80.0 percent with upward propagation of flame and 40.6 and 76.5 percent with downward propagation (*269*).

The limits of another sample of producer gas were 20.7 and 73.7 percent in a small bulb compared with 20.2 and 71.8 percent calculated by the method given on page 5 but based on limits of the individual gases in larger apparatus (*367*). A sample of nearly the same composition, tested at a later date in a similar apparatus, gave similar figures: 19.9 and 72.5 percent (*368*).

The limits of a "theoretical producer gas," with downward propagation of flame in a Bunte burette, were 39.8 and 69.6 percent (*270*).

The compositions of the various samples of producer gas used were:

Reference	(*269*)	(*367*)	(*368*)	(*270*)
Carbon dioxide	2.8	6.2	6.0	....
Oxygen	....	....	0	....
Hydrogen	4.6	12.4	14.6	....
Carbon monoxide	30.9	27.3	27.6	34.9
Methane	....	.7	Trace	....
Nitrogen	61.7	53.4	51.8	65.1

The very marked differences in the lower limits are partly due to the differences in experimental methods, but mainly to the variation of hydrogen content between the samples.

PRODUCER GAS IN OTHER ATMOSPHERES

Atmospheres of Air and Water Vapor.—The limits of mixtures of producer gas (composition given in previous table under reference *368*) and air, standing over water in a 350-cc. spherical vessel and ignited near the water surface, have been determined at various temperatures. As the temperature rises, and consequently the water-vapor content also, the lower limit rises slowly and the higher limit falls rapidly. When about 43 percent of water vapor is present the limits coincide at about 27 percent of producer gas (*368*).

OIL GAS

The limits of a gas of unspecified composition, perhaps in a eudiometer tube, are given as 6 and 13.4 percent (*120*).

OIL GAS AND ACETYLENE

The limits of a mixture of 75 percent oil gas and 25 percent acetylene in air, observed perhaps in a eudiometer tube, are given as 4 and 15.5 percent (*120*).

VARIOUS FUEL GASES

The limits of "explosibility" of various fuel gases in air were determined in a tube 4 cm. in diameter and 79.6 cm. in length, one end being permanently closed and the other sealed with a diaphragm of varnished paper. Ignition was obtained by a coil of iron wire that was caused to glow by a 10- to 15-ampere current. The results were (*103*):

Composition	Coal gas (?)	Coal gas (?)	Town gas (?)	Water gas (?)	Semi-water gas (?)	Producer gas (?)
Carbon dioxide	3.2	2.0	3.6	4.2	4.4	3.6
Unsaturated hydrocarbons	4.4	3.6	2.6	......	......	......
Oxygen	1.0	.4	.4	.4	.4	.4
Carbon monoxide	9.0	8.8	17.6	40.4	34.2	29.2
Hydrogen	47.8	52.4	45.4	43.0	34.4	10.0
Methane	27.0	27.0	18.6	......	......	......
Nitrogen	7.6	5.8	11.8	12.0	26.6	56.8
Lower limit c_c^r	8.5	9.5	10.4	13.5	16.0	31.0
Higher limit c_c	25.0	29.0	30.5	68.5	70.5	74.0

COKE-OVEN GAS AND AMMONIA

The limits of some mixtures of coke-oven gas and ammonia were found to be nearly in accordance with Le Chatelier's law; but the mixture used as synthesis gas for the production of HCN had a somewhat greater higher limit than the calculated figure (*280*).

ETHYLENE AND (1) ETHYLENE DICHLORIDE, (2) ETHYLENE DIBROMIDE, (3) n-BUTYL BROMIDE

The limits of these pairs of mixtures in air, for downward propagation of flame in a tube 1.6 cm. in diameter, have been determined (*217*).

SOME HYDROCARBONS: ETHER; ETHYL CHLORIDE AND BROMIDE; DIETHYL SELENIDE; TIN TETRAMETHYL; LEAD TETRAMETHYL

Limits of the following pairs of mixtures, in various proportions, have been determined with downward propagation of flame in a tube 5 cm. wide and 65 cm. long: Methyl cyclohexane and ethyl chloride (*246*); "hydrocarbon" (isoheptane and dimethyl cyclohexane) and ethyl bromide (*246*); "hydrocarbon" (isoheptane and dimethyl cyclopentane) and diethyl selenide, also with tin tetramethyl and lead tetramethyl (*247*); ethyl ether and ethyl bromide (*246*); ethyl ether and methyl iodide (*246*); ethyl ether and tin tetramethyl (*247*); and ethyl ether and lead tetramethyl (*247*). The results are of the general type shown in figure 4 (p. 13) and were interpreted similarly.

CYCLOHEXANE; BENZENE; ETHYL ALCOHOL

The lower limits of mixtures of cyclohexane, benzene, and ethyl alcohol (in pairs or together) agree fairly well with Le Chatelier's law at temperatures of 100° to 250° C. (*21, 23*).

TOLUENE; ETHYL ALCOHOL; ETHYL ACETATE

The lower limits of mixtures of toluene, ethyl alcohol, and ethyl acetate (in pairs or together), with upward propagation of flame in a closed tube 10.2 cm. in diameter and 96 cm. in length, agree fairly well with the figures calculated by Le Chatelier's law (139).

Influence of Temperature.—Under the same conditions, the lower limit of a mixture containing 39 percent toluene, 6 percent ethyl alcohol, and 55 percent ethyl acetate fell from 1.76 percent at 24° C. to 1.44 percent at 200° (139).

METHYL CYCLOHEXANE; ALCOHOL; ETHER

The lower limits of mixtures of methyl cyclohexane, ethyl alcohol, and ethyl ether, in pairs and together, have been determined with downward propagation of flame in a tube 5 cm. in diameter and 70 cm. in length. The results agree with those calculated by Le Chatelier's law (319).

GASOLINE; ALCOHOLS; ETHER

Series of observations with ethyl alcohol-gasoline-air and ethyl alcohol-gasoline-ether-air mixtures in a 2,300-cc. vessel at 50° and 90° C. showed fair agreement with Le Chatelier's law. The results, expressed in cubic centimeters of liquid vaporized in 1,000 cc. of air, are probably too high throughout, as the result for pure alcohol was undoubtedly too high (20).

In the same apparatus the limits of isopropyl alcohol-gasoline mixtures nearly obeyed Le Chatelier's law (231).

BENZENE AND TOLUENE

The lower and higher limits of mixtures of benzene and toluene in air in a closed tube 5 cm. in diameter and 150 cm. in length, with upward, horizontal, and downward propagation of flame, agreed closely with the values calculated by Le Chatelier's formula (355).

BENZENE AND ETHYL ALCOHOL

The lower limits of mixtures of benzene and ethyl alcohol in air, with upward propagation of flame in a tube 5 cm. in diameter and 150 cm. in length, open at the firing end, deviate somewhat from the values calculated by Le Chatelier's formula (164).

Influence of Temperature.—The lower limits of mixtures of benzene and ethyl alcohol agree fairly well with Le Chatelier's law at temperatures from 100° to 250° C. (21, 23).

BENZOLE; METHYL ALCOHOL; ETHYL ALCOHOL; BENZOLE; ETHYL ALCOHOL; "ESSENCE TOURISME"

Curves A and B in figure 62 show the lower limits of these mixtures, respectively, with downward propagation of flame in a 2½-liter bottle at various temperatures (366). The abscissas represent cubic centimeters of liquid vaporized per liter of gaseous mixture at the temperatures of the experiments. From the density of the liquid mixtures it would be possible to calculate the volumetric composition in the gaseous state. The curves for limits drawn from the calculated figures would be more nearly vertical; that is, the lower limit would be less affected by change of temperature than the curves might suggest at first sight. These curves help to explain why it is more difficult to start a cold internal-combustion engine when the fuel is mainly alcoholic than when it is mainly a light hydrocarbon mixture.

The benzole used in the above experiments distilled between 78° and 110° C. (86 percent below 90°); 87 percent was benzene. The essence distilled between 58° and 179° C.; 92.35 percent was saturated hydrocarbons and the remainder aromatic hydrocarbons.

The lower limits of a mixture of benzene, methyl alcohol, and ethyl alcohol at 100° to 250° C., with downward propagation of flame in a 2½-liter bottle, agreed with the limits calculated by Le Chatelier's law within 11 percent (21).

The lower limits (expressed as cubic centimeters of liquid evaporated in 100 liters of the mixture) of various French gasolines and mixtures, with downward propagation of flame in a 2½-liter bottle (21), are given in table 41.

METHYL ALCOHOL AND ETHYL ALCOHOL

Lower and higher limits of mixtures of methyl and ethyl alcohol in air, with downward propagation of flame in a 2-liter cylinder at 75° C., agreed with the values calculated by Le Chatelier's formula (230); however, all the values are probably too high. Another observer (365) found that the lower limits of a 50:50 mixture of the two alcohols were 0.7 to 0.3 less than those calculated over the range 50° to 250° C. under similar conditions.

Influence of Water.—The lower limits of mixtures of water and the two alcohols rise steadily as the quantity of water increases from 0 to 60 percent by weight, but the quantity of the mixed alcohols is approximately constant in the limit mixture. With 80 percent of water it was difficult to inflame any mixture of the vaporized liquid and air at 105° C., and with 85 percent inflammation was virtually impossible (230).

TABLE 41.—*Lower limits of various French gasolines and mixtures*

Temperature, ° C.	Gasoline and benzole mixtures			Aviation gasoline, ethylated	Gasoline, 75; alcohol, 25	"Tourisme" gasoline	
						"Esso"	"Azur"
	Proportions	80 : 20	60 : 40	40 : 60				
	$d\frac{18°}{4°}$	0.750	0.779	0.806	0.725	0.738	0.741	0.756
	Octane no.	73	82	93	80	91	78.5	80
100		4.35	4.15	3.95	4.55	4.85	4.55	4.60
150		3.55	3.45	3.35	3.80	4.15	3.70	3.80
200		3.00	2.95	2.75	3.15	3.50	3.00	3.15
250		2.55	2.40	2.25	2.55	2.75	2.50	2.55
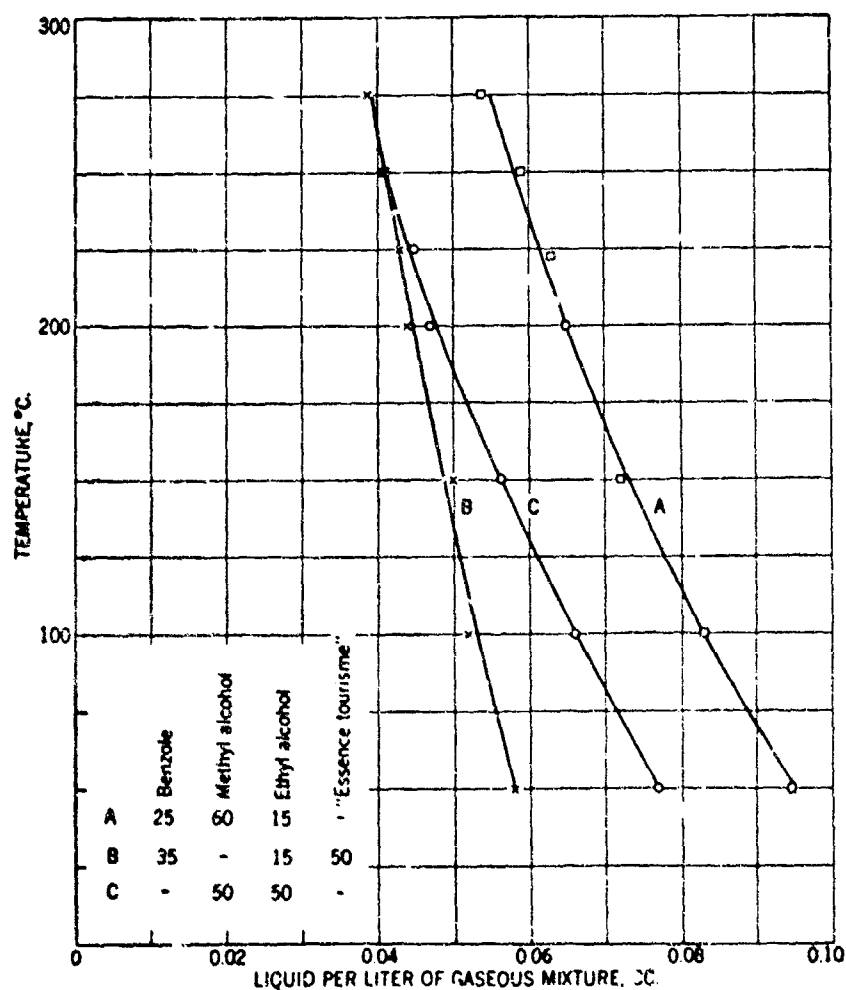
FIGURE 62.—Influence of Temperature on Lower Limits of Certain Liquid Fuels.

Influence of Temperature.—Curve C (fig. 62) shows the influence of temperature on the lower limit of a mixture of equal parts (presumably by weight) of methyl and ethyl alcohols (366). The curve would be less steep if the results were based on abscissas representing the volumetric composition of the gas mixture.

METHYL ALCOHOL AND ETHER; METHYL ALCOHOL AND ACETONE; ETHYL ACETATE AND BENZENE; ACETALDEHYDE AND TOLUENE; ETHYL NITRITE AND ETHER

The lower limits of methyl alcohol-ether, methyl alcohol-acetone, ethyl acetate-benzene, acetaldehyde-toluene, and ethyl nitrite-ether mixtures in air were determined in closed tubes 5 cm. in diameter and 150 cm. in length. The results agreed closely with Le Chatelier's law. No figures are quoted in the original communication (355).

For mixtures of methyl alcohol, acetone, and air the law has been shown to apply to higher as well as lower limits by experiments in a closed 2-liter spherical flask with ignition in the lower part of the flask (76).

ETHYL ALCOHOL AND ETHER; ACETONE AND ETHER

The lower limits of ethyl alcohol-ether-air and acetone-ether-air mixtures in closed tubes 5 cm. in diameter and 150 cm. in length agreed well with the values calculated by Le Chatelier's formula with upward, horizontal, and downward propagation of flame. The higher limits agreed closely with downward propagation, but with upward or horizontal propagation they differed greatly from the calculated values; these differences are ascribed to the irregular intervention of the "cool flame" of ether. Details of the results are given in the original references (319, 355, 361).

Large-scale experiments have been made with a mixture of ethyl alcohol and ether in the proportion of 1 : 3 by weight, vaporized into air and into mixtures of air with carbon dioxide and with nitrogen. The experimental vessel
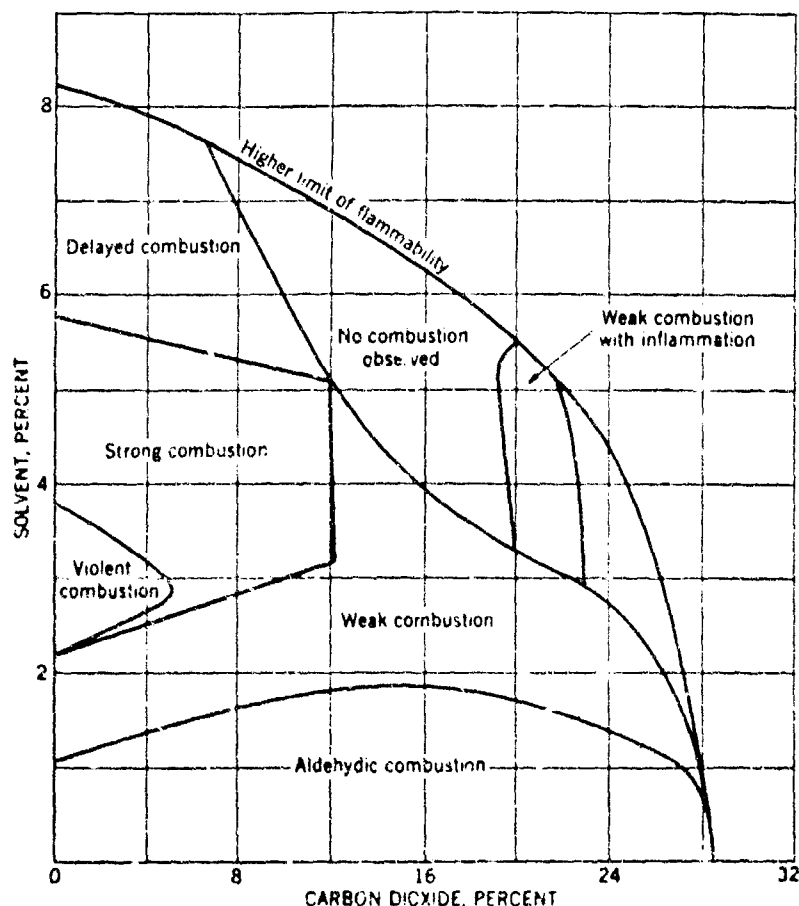
FIGURE 63.—Limits of Flammability of Solvent (Ether : Alcohol = 3 : 1) in Mixtures of Air and Carbon Dioxide.

was a section, 3.8 meters in length, at the end of a horizontal tubular steel gallery 20 meters in length and 1.68 meters in diameter. Various types of ignition were employed, all at the center of the experimental section. One end of the section (the end of the gallery) was closed permanently; the other was closed by a paper diaphragm. The nature of an ignition was judged by the sound, appearance of flame, bursting and burning of the paper diaphragm, pressure recorded on a manometer, and aldehydic odor that was sometimes developed.

The nature of the results recorded when guncotton was used as the source of ignition in the vapor in mixtures of air and carbon dioxide is shown in figure 63. When nitrogen was used in place of carbon dioxide, the limit curve was less steep and met the axis at about 38 percent nitrogen. With other means of ignition (fulminate, induction-coil spark, and fusion of a tungsten filament) the limits for weak combustions differed considerably from those in the figure. It is evident that, in spite of the large volumes of mixture used, the limits for self-propagation of flame were not obtained, doubtless because the local effects of the igniters could not be distinguished, by any available means, from self-propagating inflammation. However, as a general description of the phenomena in relation to the experimental conditions, the results are of value (*40*).

The lower limit of a 1 : 2 mixture of ethyl alcohol and ethyl ether, with horizontal propagation of flame throughout a pipeline about 100 meters in length and 45 cm. in diameter, is 43 grams per cubic meter (*289*).

ALCOHOL, CHLOROFORM, AND ETHER

The mixture of alcohol, chloroform, and ether commonly used to induce anesthesia gives vapors that form explosive mixtures with suitable proportions of air (*60*).

ETHYL ALCOHOL AND FURFURAL

The lower limits of two mixtures (3 : 1 and 1 : 3) of ethyl alcohol and furfural in air, with upward propagation of flame in a tube 5 cm. in diameter and 150 cm. in length, open at the firing end, deviate somewhat from the values calculated by Le Chatelier's formula (*164*).

ETHYL ALCOHOL AND ACETONE

The lower limit of a 4 : 1 mixture of ethyl alcohol and acetone in air, with upward propagation of flame in a tube 5 cm. in diameter and 150 cm. in length, open at the firing end, was nearly in agreement with the value calculated by Le Chatelier's formula (*164*).

ETHER AND ACETALDEHYDE

The lower limits of mixtures of ether and acetaldehyde in air in closed tubes 5 cm. in diameter and 150 cm. in length showed good agreement with the values calculated by Le Chatelier's formula, with upward and downward propagation of flame; also the higher limits, with downward propagation. The higher limits with upward propagation are definitely lower than those calculated. Both ether and acetaldehyde give rise to "cool flames" in the richer mixtures, and the higher limits reported are those of the "cool flames." The propagation of the "cool flame" by either constituent is not assisted by that of the other to the extent that an additive law would indicate (*355*).

ACETONE AND METHYL ETHYL KETONE

Observations with mixtures of acetone and methyl ethyl ketone in air in closed tubes 5 cm. in diameter and 150 cm. in length showed close agreement with the values calculated by Le Chatelier's formula for both limits, with horizontal and downward propagation of flame. With upward propagation, the lower limits were slightly higher than those calculated; the higher limits were several tenths of 1 percent higher than those calculated (*355*).

PARAFFIN-HYDROCARBON HALIDES

The limits of the following mixtures have been determined in air in a 2½-liter bell jar, with electric-spark ignition: Methyl chloride and ethyl chloride, methyl chloride and methyl bromide, and methyl bromide and ethyl chloride. All mixtures of each pair are capable of violent explosion when mixed with appropriate amounts of air. The observed limits differ appreciably from those calculated by Le Chatelier's formula (*132*).

SOME MIXED SOLVENTS FOR LACQUERS

Table 42 gives lower limits, in grams per liter, of mixtures of hydrocarbons, esters (active nitrocellulose solvents), and alcohols. The limits were determined with upward propagation of flame in a closed tube 25 cm. in length and 2.5 cm. in diameter, with central ignition (*294*).

MISCELLANEOUS MIXTURES CONTAINING FLAMMABLE GASES

Table 43 includes mixtures not mentioned elsewhere in this bulletin and containing various

proportions of flammable constituents. Their compositions are stated, together with the results of calculations (p. 5) which show whether they can form flammable mixtures with air, and if so in what proportions the mixtures are flammable (137).

TABLE 42.—Composition and limits of mixed solvents

Composition	1	2	3	4	5	6	7	8
Benzene	50	60	20			20		
Toluene			40	60	60	40	30	30
V. M. P. naphtha							30	
Ethyl acetate	50	30	15	15		10		
Butyl acetate			15		15	10		
Butyl propionate				15	15	10	30	40
Ethyl alcohol		10	5	5				
Butyl alcohol			5	5	10	10	10	30
Lower limit, grams per liter	0. 070	0. 057	0. 071	0. 098	0. 082	0. 062	0. 059	0. 077

TABLE 43.—Composition and limits of flammability of miscellaneous gases

Sample	Type	Composition, percent								Limits of flammability, percent	
		CO_2	C_2H_4	O_2	H_2	CO	CH_4	C_2H_6	N_2	Lower	Higher
1	Soil gas	16. 6	0. 3	1. 0	0. 2	0	3. 2	0	78. 7	(1)	(1)
2	do	9. 6	0	5. 9	0	0	. 2	0	84. 3	(1)	(1)
3	do	6. 8	. 7	6. 0	0	0	10. 5	0	76. 0	49. 0	55. 0
4	Soil + natural gas	8. 0	. 2	5. 9	0	0	18. 4	5. 0	62. 5	20. 0	39. 0
5	do	. 6	0	6. 7	0	0	52. 5	12. 1	28. 1	7. 0	22. 0
6	Sewage gas	25. 2	0	. 1	0	0	67. 8	0	6. 9	7. 5	19. 0
7	Fermentation gas, cellulose	79. 1	6	0	6. 2	0	14. 7	0	0	26. 5	38. 5
8	Fermentation gas, grain	65. 4	0	0	32. 5	0	. 1	0	2. 0	13. 0	66. 0
9	Gases from heated insulation	1. 9	17. 4	0	28. 5	2. 2	45. 3	. 3	4. 4	4. 5	21. 5
10	Gases from burning wood	6. 4	. 6	9. 4	0	3. 5	. 3	0	79. 8	(1)	(1)
11	Gases from burning paper	7. 6	1. 2	7. 7	0	6. 2	0	0	77. 3	(1)	(1)
12	Soil + coal gas	3. 0	1. 2	12. 2	7. 1	4. 4	11. 8	2. 2	58. 1	18. 0	66. 5
13	Gases from explosives, TNT	6. 4	0	0	26. 9	53. 2	. 2	0	13. 3	9. 5	72. 0
14	do	1. 5	0	0	19. 9	60. 7	2. 3	0	15. 6	10. 0	67. 0

1 Nonflammable.

PART V. SUMMARY OF LIMITS OF FLAMMABILITY

Tables 44 and 45 contain selected values for the limits of flammability of single gases and vapors and of some industrial mixtures in air and in oxygen at ordinary temperatures and pressures. Table 46 contains selected limits in nitrous and nitric oxides.

The last two columns of tables 44 and 45 give the oxygen percentage, in mixtures of flammable gas (or vapor) and air with (a) nitrogen and (b) carbon dioxide, below which no mixture is flammable.

The values in boldface observed with upward propagation of flame in large vessels, open at their lower ends, are chosen as those most useful for reasons given earlier. The other figures represent experiments with mixtures contained in closed or small vessels; they are therefore not applicable with certainty to conditions in which normal pressure is maintained during the passage of flame. Reference to the text will define more exactly the conditions of observation.

Many of the higher limits, and a few of the lower limits, of the vapors of liquids could only be determined by raising the temperature sufficiently to raise the vapor pressure to the extent necessary to reach the limit composition. The limit given, therefore, applies to the experimental temperature, which is quoted in the text if it is stated in the original source of the information.

Further information about the limits of gases and vapors will be found in the text; the data are not suitable for inclusion in the tables but may be useful if the conditions of determination are kept in mind.

Information on limits in other atmospheres and on the influence of pressure and temperature and the effect of turbulence will also be found in the text.

The limit figures in table 45 apply only to particular samples; analytical data will be found in the text. By the use of Le Chatelier's law the limits of similar mixtures can be calculated.

TABLE 44.—*Summary of limits of flammability of individual gases and vapors in air and in oxygen*

Gas or vapor	Limits in air, percent				Limits in oxygen, percent				Oxygen percentage below which no mixture is flammable	
	Lower		Higher		Lower		Higher		Nitrogen as diluent of air	Carbon dioxide as diluent of air
INORGANIC										
Hydrogen	**4.0**	4.0	**75**	75	.....	4.0	**94**		5.0	5.9
Deuterium		5		75	.....	5		95		...
Ammonia		15		28	.....	15		78		...
Hydrazine		4.7	.....	100	.....					...
Hydrogen sulfide		4.3	.....	45	.....					...
Hydrogen cyanide		6		41	.....					...
Cyanogen		6		32	.....					...
Carbon disulfide	1.25	.....	**44**	50	.....					...
Carbon oxysulfide		12	.....	29	.....					...
Carbon monoxide	12.5	.....	**74**		.....	15.5	.....	94	5.6	5.9
Chlorine monoxide		23.5	.....	100	.....					...

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TABLE 44.—*Summary of limits of flammability of individual gases and vapors in air and in oxygen*—
Continued

Gas or vapor	Limits in air, percent				Limits in oxygen, percent				Oxygen percentage below which no mixture is flammable	
	Lower		Higher		Lower		Higher		Nitrogen as diluent of air	Carbon dioxide as diluent of air
HYDROCARBONS										
Methane	5.3	(5.0)	14	15	5.1		61		12.1	14.6
Ethane	3.0		12.5	15	3.0		66		11.0	13.4
Propane	2.2		9.5		2.3		55		11.4	14.3
Butane	1.9		8.5		1.8		49		12.1	14.5
Isobutane	1.8		8.4		1.8		48		12.0	14.8
Pentane	1.5	1.4	7.8						12.1	14.4
Isopentane	1.4		7.6							
2-2 Dimethyl propane	1.4		7.5							
Hexane	1.2		7.5						11.9	14.5
Dimethyl butane	1.2		7.0							
2-Methyl pentane	1.2		7.0							
Heptane	1.2	1.1	6.7							
2-3 Dimethyl pentane	1.1		6.7							
Octane	1.0									
Iso-octane	1.1	1.0		6.0						
Nonane		.8								
Tetramethyl pentane	.8		4.9							
Diethyl pentane		.7		5.7						
Decane	.8			5.4						
Ethylene	3.1	2.7	32	34	3.0		80		10.0	11.7
Propylene	2.4	2.0	10.3	11	2.1		53		11.5	14.1
Butylene	2.0		9.6							
Butene-1	1.6		9.3		1.8		58		11.6	14.0
Butene-2	1.8		9.7		1.7		55			
Isobutylene	1.8		8.8							
b-n-Amylene	1.5	1.4	8.7							
Butadiene	2.0		11.5						10.	13.1
Acetylene	2.5	(2.3)		81						
Benzene	1.4		7.1						11.2	13.9
Toluene	1.4	1.3		6.7						
o-Xylene		1.0		6.0						
Ethyl benzene	1.0									
Styrene		1.1		6.1						
Butyl benzene		.8		5.8						
Naphthalene		.9		5.9						
Cyclopropane	2.4		10.4		2.5		60		11.7	13.9
Ethyl cyclobutane	1.2		7.7							
Ethyl cyclopentane	1.1		6.7							
Cyclohexane	1.3		8							
Methyl cyclohexane	1.2									
Ethyl cyclohexane	.9		6.6							
ALCOHOLS										
Methyl alcohol	7.3	6.7		36					10.3	13.5
Ethyl alcohol	4.3	3.3		19						
n-Propyl alcohol		2.1		13.5						
Isopropyl alcohol		2.0		12						
n-Butyl alcohol		1.4		11.2						
Amyl alcohol		1.2								
Furfuryl alcohol		1.8		16.3						
Allyl alcohol		2.5		18.0						
Propylene glycol		2.6		12.5						
Triethylene glycol		.9		9.2						

TABLE 44.—*Summary of limits of flammability of individual gases and vapors in air and in oxygen*—Continued

Gas or vapor	Limits in air, percent				Limits in oxygen, percent				Oxygen percentage below which no mixture is flammable	
	Lower		Higher		Lower		Higher		Nitrogen as diluent of air	Carbon dioxide as diluent of air
ETHERS										
Methyl ether	3.4	......	18	27	......	3.9	......	61		
Ethyl ether	1.9	1.7	48	......	2.0	2.1	......	82		
Ethyl n-propyl ether	1.9		24	......	2.0	......	78			
Isopropyl ether	1.4	1.3	21	......			69			
Vinyl ether	......	1.7	27	28	......	1.8	......	85		
Ethylene oxide	3.0	3.6	80	100						
Propylene oxide	2.1	......	21.5							
Dioxane		2.0	......	22						
Trioxane		3.6	......	29						
Acetal	1.6	......	10.4							
Methyl cellosolve		2.5	......	19.8						
Ethyl cellosolve		1.8	......	14.0						
Butyl cellosolve		1.1	......	10.6						
Diethyl peroxide		2.3								
ALDEHYDES										
Acetaldehyde	4.1	......	55		......	4	......	93		
Paraldehyde		1.3								
Butyraldehyde	2.5									
Acrolein	2.8		31							
Croton aldehyde		2.1	......	15.5						
Furfural	2.1									
KETONES										
Acetone	3.0	2.5	11	13			......	13.5	15.6	
Methyl ethyl ketone		1.8	......	10						
Methyl propyl ketone		1.5	......	8						
Methyl butyl ketone		1.3	......	8						
Methyl isobutyl ketone		1.4	......	7.5						
Cyclohexanone		1.1								
Isophorone		.8	......	3.8						
ACID; ANHYDRIDES										
Acetic acid		5.4								
Acetic anhydride		2.7		10						
Phthalic anhydride		1.7		10.5						
ESTERS										
Methyl formate	5.9	5.0	20	23						
Ethyl formate	2.7		13.5	16.4						
Butyl formate		1.7		8						
Methyl acetate		3.1		16						
Ethyl acetate	2.5	2.2	9	11						
Vinyl acetate	2.6		13.4							
Propyl acetate	2.0	1.8	......	8						
Isopropyl acetate		1.8		8						
Butyl acetate	1.7	1.1		7.6						
Amyl acetate		1.1								
Methyl cellosolve acetate		1.7		8.2						
Methyl propionate	2.45	......	13							
Ethyl propionate	1.85		11							
Methyl lactate		2.2								
Ethyl lactate		1.5								
Ethyl nitrate	4.0									
Ethyl nitrite	4.1	3.0								

TABLE 44.--*Summary of units of flammability of individual gases and vapors in air and in oxygen—Continued*

Gas or vapor	Limits in air, percent		Limits in oxygen, percent		Oxygen percentage below which no mixture is flammable	
	Lower	Higher	Lower	Higher	Nitrogen as diluent of air	Carbon dioxide as diluent of air
PHENOLS						
Cresol	1.1					
AMINES AND IMINES						
Methylamine	4.9	20.7				
Dimethylamine	2.8	14.4				
Trimethylamine	2.0	11.6				
Ethylamine	3.5	14.0				
Diethylamine	1.8	10.1				
Triethylamine	1.2		8.0			
Propylamine	2.0	10.4				
n-Butyl amine	1.7	9.8				
Allylamine	2.2	22				
Ethylene imine	3.6	46				
OTHER NITROGEN COMPOUNDS						
Acrylonitrile	3.0	17				
Pyridine	1.8	12.4				
Nicotine	.7	4.0				
HALOGEN DERIVATIVES						
Methyl chloride	10.7	17.4	8		66	
Methyl bromide	13.5	14.5	14	19		
Methylene chloride			15.5		66	
Ethyl chloride	3.8	15.4	4.0	67		
Ethyl bromide	6.7	11.3	6.7	44		
Ethylene dichloride	6.2	16				
Vinyl chloride	4.0	22	4.0	70		
Dichloroethylene	9.7	12.8	10	26		
Trichloroethylene			10	65		
Ethylene chlorohydrin	4.9	15.9				
Propyl chloride	2.6	11.1				
Propylene dichloride	3.4	14.5				
Allyl chloride	3.3	11.1				
Allyl bromide	4.4	7.3				
2-Chloropropene	4.5	16.0	4.5	54		
n-Butyl chloride	1.8	10.1				
Isobutyl chloride	2.0	8.8				
Butyl bromide	5.2	5.6				
Chlorobutene	2.2	9.3				
Isocrotyl chloride	4.2	19	4.2	66		
Isocrotyl bromide	6.4	12	6.4	50		
n-Amyl chloride	1.6	8.6				
tert-Amyl chloride	1.5	7.4				
Chlorobenzene	1.3	7.1				
Dichlorobenzene	2.2	9.2				
MISCELLANEOUS						
Dimethyl sulfide	2.2	19.7				
Ethyl mercaptan	2.8	18.0				
Diethyl selenide	2.5					
Dimethyldichlorosilane	3.4					
Methyltrichlorosilane	7.6					
Tin tetramethyl	1.9					
Lead tetramethyl	1.8					

TABLE 45.—*Approximate limits of flammability of some complex industrial mixtures of gases and vapors in air and in oxygen*

Gas or vapor	Limits in air, percent		Limits in oxygen, percent		Oxygen percentage below which no mixture is flammable	
	Lower	Higher	Lower	Higher	Nitrogen as diluent of air	Carbon dioxide as diluent of air
Water gas	7.0	72				
Carbureted water gas	5.5	36				
Pittsburgh natural gas	4.8	13.5			12.0	14.4
Other natural gases	3.8–6.5	13–17				
Benzine	1.1					
Gasoline	1.4	7.6			11.6	14.4
Naphtha	0.8	5				
Kerosine	.7	5				
Coal gas	5.3	32	7	70	11.5	14.4
Coke-oven gas	4.4	34				
Blast furnace gas	35	74				
Producer gas	17 20–35	70	70–80			
Oil gas	4.7	33				

TABLE 46.—*Limits of flammability in nitrous and nitric oxides*

Gas or vapor	Nitrous oxide		Nitric oxide	
	Lower limit	Higher limit	Lower limit	Higher limit
Hydrogen	5.2	80	13.5	49
Ammonia	2.2	72		
Hydrogen sulfide			20	55
Carbon disulfide	1	52	4.5	59
Carbon monoxide	19	84	31	48
Methane	2.2	36	9	22
Butane	2.5	20	7.5	12.5
Ethylene	1.9 5	40	35	
Propylene	1.45	29		
Cyclopropane	1.6	30		
Ethyl ether	1.5	24		
Vinyl ether	1.4	25		
Methyl chloride	5			
Ethyl chloride	2.0	33		

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